

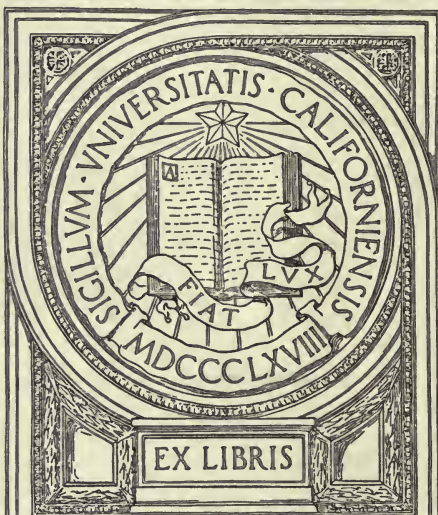
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# AN INTRODUCTION

TO THE PRACTICE OF

## COMMERCIAL ORGANIC ANALYSIS;

BEING A TREATISE ON

THE PROPERTIES, PROXIMATE ANALYTICAL EXAMINATION, AND MODES OF  
ASSAYING THE VARIOUS ORGANIC CHEMICALS AND PREPARATIONS  
EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, &c.

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES,  
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION.

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VOLUME I

CYANOGEN COMPOUNDS, ALCOHOLS AND THEIR DERIVATIVES,  
PHENOLS, ACIDS, &c.

LONDON:

J. & A. CHURCHILL, NEW BURLINGTON STREET.

1879.

THE END OF THE  
WORLD



## PREFACE.

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WHILE the libraries of chemists are replete with manuals and treatises on Inorganic Analysis, and the number of these works is being increased almost monthly, books on Organic Analysis are chiefly conspicuous by their absence; and the unfortunate chemist who requires to make an assay or analysis of a commercial organic product, is driven to seek for various items of information—often contradictory or unreliable—in the pages of one or two very imperfect works, and of a few English and foreign scientific periodicals.

It is a lamentable fact, that while our young chemists are taught to execute ultimate organic analyses, and to ring the changes on the everlasting chloro- bromo- and nitro-derivatives of bodies of the aromatic series, the course of instruction in many of our leading laboratories does not include even qualitative tests for such everyday substances as alcohol, chloroform, glycerin, carbolic acid, and quinine. As a natural consequence of this neglect, the methods for the proximate analysis of organic mixtures, and for the assay of commercial organic products, are

in a far more backward state than is justified by the great inherent difficulties of this branch of analysis. Professor A. B. Prescott, in the preface to his admirable little work on "Proximate Organic Analysis," points out that fifty years ago the workers in inorganic analysis were unprovided with a comprehensive system, but that did not prevent them from using their scanty means to gain valuable results. Nor should the fact that the existing methods of proximate organic analysis are very imperfect, prevent chemists from working in a comparatively new field—a field in which there is as much really useful treasure to be found as in the mazes of original organic research.

Having, in my own practice as a consulting chemist, repeatedly felt the need of a convenient handbook, containing all reliable information respecting the methods of assaying and analysing organic substances in common use, I presume that others will have suffered similar experiences, and hence that a work on the subject will "supply a want which has long been felt." How far I have succeeded in filling the void it is not for me to say; but I believe this volume contains many methods which have never been described under one cover before, and some which have never previously been published in the English language. I have also added not a few processes which have originated with myself, and have been tested in my own laboratory.

In the present volume, I have assumed, on the part of the reader, a knowledge of general chemical principles, and an acquaintance with the modes of mani-

pulation employed in the qualitative and quantitative analysis of inorganic bodies. Hence, I have not thought it necessary in all cases to say that precipitates must be filtered off or washed, and have made no attempt to describe the precautions desirable in employing volumetric solutions. A knowledge is also assumed of the ordinary methods of calculating the amounts of substances from the weights of the precipitates obtained, though in most cases factors are given for the convenience of the analyst.

At one time I hoped to have been able to announce that all tests and processes described in this book had been verified by myself; but, in addition to finding this labour beyond my powers, I concluded that in many cases such verifications were unnecessary. Nevertheless, in most instances in which reactions and methods were not generally accepted as reliable, or were not vouched for by some indisputable authority, I have taken care personally to verify the statements I have made, so that in the very great majority of instances the reactions and methods given may be safely relied on. The verifications actually made have extended over some years, and have resulted in the rejection as worthless of some of the statements and processes which have been copied from book to book for the last thirty or forty years.

It is with some diffidence that I have adopted a mode of diction which takes up considerable space, and I dare say critics will not be wanting to declare that I might have advantageously adopted a style which I may describe as "telegraphic." By so

doing, I might certainly have greatly condensed the information given, but I believe the advantage would have been gained at the expense of clearness.

I at one time hoped to make a single volume suffice to cover the whole ground of proximate analysis and assay of commercial organic products, but, finding that the subject rapidly grew, and that the information already compiled would become stale and lose much of its value if its publication were long delayed, I decided to publish Volume I. separately.

In the arrangement of the subject-matter, I have ignored the more obscure chemical relationships and have preferred grouping the bodies treated of in a manner which, it is hoped, will be found convenient for practical reference, though such an arrangement has necessitated some inconsistencies.

In the present volume, I have devoted an introductory chapter to the general principles and methods of organic analysis. Although the methods of ultimate analysis could scarcely be entirely omitted, I felt that I had nothing new to say on such a well-worn subject, and hence I have merely glanced at the methods employed. Some of the sections of this division, such as the one on "Solubilities," contain more novel matter. "Cyanogen and its Derivatives" naturally claimed a separate division, and I found more straggling information on this well-known subject than I at first thought possible. I have added a few methods never before published.

Of course, the consideration of the "Alcohols" demanded a separate division, though I have used the



term in a more restricted sense than has lately been common. "Neutral Alcoholic Derivatives" furnished the matter for another division. As one section of this part treats of "Compound Ethers," in strict consistency I ought therein to have considered oils and fats. There would, however, have been much practical inconvenience in such a course, and I therefore preferred to allow the section on "Oils and Fats" to form part of Volume II. The consideration of soap and the higher fatty acids is deferred for a similar reason. "Essential Oils," too, I propose shall have a future section to themselves, but I have somewhat anticipated it by sub-articles on Benzoic Aldehyde, Methyl Salicylate, Oil of Mustard, and Oil of Thyme. The next division is devoted to the consideration of "Acid Alcoholic Derivatives and Vegetable Acids."

The "Phenols," in analytical respects, possess few of the properties of the Alcohols, and I have therefore placed them in a separate division, which is conveniently followed by one on their "Acid Derivatives."

Most of the sections contain supplementary articles which could not conveniently be arranged separately, without necessitating a vast amount either of repetition or of cross reference. I have avoided both these defects as far as possible, but in many instances they were compulsory.

I have made no attempt to describe a systematic method of effecting the separation of an indefinite number of organic substances; but in numerous instances processes are described for detecting and separating the various impurities and foreign matters



liable to be associated with the bodies under consideration.

For the subject-matter of this treatise I am, of course, largely indebted to standard works on chemistry and to various scientific periodicals. Of the many sources of information which I have laid under contribution, I must, however, make special mention, amongst English periodicals, of the "Chemical News," "Analyst," "Pharmaceutical Journal," "Chemist and Druggist," and "Journal of the Chemical Society;" among standard works I have culled largely from the pages of Watts' "Dictionary of Chemistry," the new "Manufacturing Chemistry" edited by Chas. Vincent, Muter's "Pharmaceutical Chemistry," Chevalier and Baudrimont's "Dictionnaire des Altérations et Falsifications," Prescott's "Proximate Organic Analysis," and Woodman and Tidy's "Forensic Medicine and Toxicology." Various other works have also furnished me with valuable material.

In conclusion, I must thank the friends to whom I am indebted for the revision of some of the principal articles, and by whose kind assistance the book has greatly profited. Should my present efforts meet with a favourable reception, I shall be encouraged to ask their assistance in compiling the second volume.

ALFRED H. ALLEN.

SHEFFIELD, *June* 1879.

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## INTRODUCTION.

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THE term Analysis, though originally meaning a separation or splitting up of a substance into its constituent parts, has now become greatly extended in its application, so that a process of chemical analysis may mean either—

1. A true analysis, or separation into constituent parts ;
2. A qualitative identification or recognition of a substance sought for ; or,
3. A quantitative determination of the amount of a particular body with more or less accuracy.

When the quantitative determination is limited to one or two important bodies which constitute the valuable or active constituents of a more complex substance, the analytical process is frequently called an *assay*. It is in this sense the term assay is employed throughout this work.

Very frequently the chemical examination of a substance includes the search for, or determination of impurities and foreign constituents accidentally present or purposely added. The nature of the foreign ingredients will, of course, largely depend upon that of the substance, and cannot be generally described. They may, however, be conveniently classified under the following heads :—

a. Foreign bodies naturally associated with the main substance, and not readily removed during the process of preparation. *Examples* : acetone in wood spirit, hydrocyanic acid in bitter-almond oil, and cresylic acid in carbolic acid.

b. Foreign bodies introduced during the process of manufacture, and not subsequently (perfectly) eliminated. *Examples* :

cyanate and carbonate of potassium in commercial cyanide, sulphuric acid and lead in organic acids, alcohol in ether.

c. Foreign bodies legitimately added in small quantity, to confer some special property on the main substance. *Examples*: mineral acids in hydrocyanic acid, alcohol in chloroform.

d. Foreign bodies produced by the spontaneous change of the main substance. *Examples*: benzoic acid in bitter-almond oil, metaldehyde in aldehyde, ethyl acetate in tincture of acetate of iron.

e. Adulterants purposely added to increase the weight or bulk, or to confer some special property, or to conceal weakness or inferiority of the main substance. *Examples*: water in spirituous and vinous liquids, tartaric acid in citric acid, nitrobenzene in bitter-almond oil.

For the chemical examination of organic bodies a great variety of methods are employed, the details of which will be given under the proper heads, but the following general principles are frequently applied for the recognition and quantitative examination of organic bodies:—

1. A preliminary examination of the leading characters of the body, such as its colour, taste, smell, and microscopic appearance.

2. An accurate study of the physical properties of the body, including the determination of its density, melting and boiling points, action on polarised light, &c.

3. An examination of the solubility of the substance in various menstrua.

4. An ultimate or elementary analysis of the body.

5. The production and examination of definite compounds or products of decomposition of the substance.

The above methods of examination are chiefly applicable to the recognition of comparatively pure substances, but the principles involved are continually employed in the practical proximate analysis and chemical examination of organic bodies. Thus, by the varied behaviour of the associated

bodies, when examined by one or more of the above methods, we effect a practical recognition, determination, or separation of the constituents of the sample.

It is not proposed to describe the above methods of examination in detail, as it would involve lengthy descriptions of processes with the general nature of which the user of this book is presumably acquainted. In most cases, the outline of the method of examination is alone indicated. Sufficient working details for the use of any one versed in simple chemical manipulation are given under the special articles devoted to the examination of the various organic preparations employed in commerce.

## 1. PRELIMINARY EXAMINATION.

When the organic body to be examined is of wholly unknown nature, a judicious preliminary examination will often throw much light on its nature. The following points should not be lost sight of:—

(a) **Colour.**—The colours of organic bodies are not as a rule very characteristic, but there are some very remarkable exceptions. As a rule, blue vegetable colouring matters are rendered red by acids, and the blue colour is restored or changed to green by ammonia. Indigo is not affected. Vegetable yellows are generally turned brown by alkalies, and the colours restored by acids. The examination of the absorption spectra of coloured organic substances often furnishes most valuable information.

(b) **Taste.**—This character must be observed with extreme caution, as many organic bodies are intensely poisonous. The safest way is to make a weak aqueous or alcoholic solution of the substance, and taste a drop of the liquid cautiously. Acids are, as a rule, sour or astringent in taste. Alkaloids are usually bitter. The sugars and glycerin are sweet.

(c) **Smell.**—This character is often very peculiar, notably so in the case of the neutral alcoholic derivatives.



(d) **Microscopic appearance.**—In the case of solid bodies an examination under the microscope is often extremely useful. As a rule, the use of a high power is neither necessary nor desirable. The micro-polariscope affords valuable means of identifying the starches.

(e) **Effect of heat.**—The behaviour of organic substances on heating is often highly characteristic. Solids should be heated in a small dry test-tube. It is well to make an experiment first on a piece of platinum foil. A few substances explode violently when heated. On ignition in the air all organic substances other than those containing metals are completely consumed. Sometimes volatilisation occurs without darkening; in other cases, a more or less voluminous residue of carbon is left, which is sometimes only burnt away with great difficulty. Salts of organic acids containing metals of the alkalis or alkaline earths usually leave these metals as carbonates on being ignited in the air. Hence the presence of carbonate in the ash indicates the previous presence of an organic acid. Volatile heavy metals, such as arsenic or mercury, are wholly driven off on igniting substances containing them, but most heavy metals remain on ignition either as oxides or in the metallic state.

The density, boiling and melting points, and other physical properties of the substance may be roughly noted as part of the preliminary examination, but these characters are referred to at greater length in the next section.

## 2. STUDY OF PHYSICAL PROPERTIES.

**Specific gravity.**—The specific gravity of an organic solid or liquid is often a most valuable criterion of its identity or purity. Unlike the determination of the density of a vapour it is frequently applicable to the accurate estimation of a substance in solution or in admixture with another body, and in other cases it may be used to discriminate between different isomeric bodies of the same percentage composition.

Instances of its value are to be found in the determination of alcohol or glycerin in admixture with water, and in the discrimination of tartaric and racemic acids.

A table giving the specific gravities of various organic bodies will be found on pages 12 and 13, of ethers on page 140, of chlorinated derivatives of ethane on 158, and of fatty acids on page 211.

The hydrometer is an instrument so well known that its use requires no detailed description. The graduation of hydrometers is usually conducted on one of three systems. The graduations may indicate the actual density of the liquid as compared with water, or the stem of the hydrometer may be graduated in degrees of Twaddell or Beaumé. Twaddell's hydrometer applies only to liquids heavier than water. The indications are translated into actual densities by multiplying degrees Twaddell by 5, and adding 1000. Thus, a liquid which marks  $68^{\circ}$  Twaddell, has an actual density of  $68 \times 5 + 1000 = 1340$ , compared with water as 1000.

Beaumé's hydrometer is but little used in England. On this scale,  $15^{\circ}$  is the point to which the hydrometer sinks in a solution of 15 parts of common salt in 85 of water. The interval between this point and the zero is divided into 15 equal parts, and a scale of similar equal parts extended as far as is necessary. For liquids lighter than water, water is  $10^{\circ}$ , and the zero is found by immersing the instrument in a solution of 10 parts of common salt in 90 of water.

In Cartier's hydrometer,  $22^{\circ}$  corresponds with  $22^{\circ}$  Beaumé, but above and below this point the degrees are diminished in the ratio of 16 to 15.

In Beck's hydrometer,  $0^{\circ}$  corresponds to the density of water, and  $30^{\circ}$  to a density of .850, and the scale is divided into equal parts above and below the zero point as far as desirable.

The graduation of hydrometers, even when sold by first-rate firms, is often very far from accurate. Hence, such instruments should never be trusted till their indications have been carefully verified.

For general use in the laboratory, the specific gravity bottle is the most serviceable instrument. It should not be trusted to contain the amount of water marked on it, but should be carefully filled with distilled water at the temperature at which the sample of liquid is to be compared (usually  $15.5^{\circ}\text{C.} = 60^{\circ}\text{F.}$ ), and the weight of contained water ascertained. The density of the sample of liquid is found by dividing the weight of it which the bottle will contain by the weight of water contained at the same temperature. When the liquid is miscible with water, the wet bottle may be rinsed out once or twice with a few drops of the sample; when the liquid is insoluble or nearly so in water, the bottle should be rinsed once or twice with alcohol and then with ether, the last traces of the latter being got rid of by a current of dry air from a bellows or by sucking the ether vapour from the warmed bottle by means of a glass tube.

A good instance of the method of taking the specific gravity of a liquid is given on page 83.

A very useful and accurate method of taking the specific gravity of liquids, especially when but small quantities of material are at disposal, is by a method described by Dr Sprengel,\* in which a small U-shaped apparatus terminating in horizontal capillary tubes is substituted for the ordinary specific gravity bottle. It may be filled with liquid with extreme ease, and the regulation of the quantity of contained liquid is also very easily effected. The results are extremely accurate.

Unfortunately, much confusion has crept into the mode of stating specific gravities. Thus, if ether be stated to have a density of  $.7185$  at  $17.5^{\circ}\text{C.}$ , there is really no certainty as to what is intended to be understood by the statement. It may be meant that a bottle which held 100 grammes of water at  $17.5^{\circ}$ , held only  $71.85$  grammes of ether. Or the bottle may have held 100 grammes of water at  $15.5^{\circ}\text{C.}$  ( $= 60^{\circ}\text{F.}$ ), at  $15.0^{\circ}\text{C.}$ , at  $4^{\circ}$ , or at  $0^{\circ}\text{C.}$  In many

\* *Journ. Chem. Soc.* 1873, p. 577. The apparatus is made by Cetti.



instances it is quite uncertain whether the recorded densities refer to a comparison with an equal bulk of water at the same temperature as the liquid was weighed at, or any one of the temperatures just given. As a rule, when the density of a substance is stated to be so much at  $15.5^{\circ}\text{C.}$  ( $= 60^{\circ}\text{F.}$ ), it may be regarded as certain that the unit of water was weighed at the same temperature, but in the other cases it is by no means certain what is meant. This fertile source of error has been commented on in an able manner by Dr W. A. Tilden.\*

The specific gravity of organic solids is best taken by introducing some fragments or powder into a specific gravity bottle and ascertaining the weight in grammes taken. The bottle is next filled with water, petroleum, or some liquid of known density having no solvent action on the solid to be examined, and the weight is then again observed. The increase gives the weight of the contained liquid, and this multiplied by its known density, gives its volume. This subtracted from the known capacity of the bottle in c.c. gives the measure of the solid, which, divided into its weight in grammes, gives the density compared with water as unity. Care must be taken to avoid the adherence of air bubbles to the solid. Agitation will generally suffice to get rid of them.

The determination of the vapour density of an organic body often furnishes a most complete test of its formula. In all cases in which decomposition of the substance does not occur, the density of the vapour, compared with that of hydrogen at the same temperature and pressure, is *one-half* the molecular weight.

Thus the density of the vapour of alcohol is 23 times that of hydrogen, which gives 46 as the molecular weight, and establishes the formula  $\text{C}_2\text{H}_6\text{O}$ . Similarly, benzene vapour is 39 times heavier than hydrogen, which corresponds with the formula  $\text{C}_6\text{H}_6$ , and negatives the possibility of  $\text{CH}$ ,  $\text{C}_2\text{H}_2$ , or other simpler formula expressing the true constitution of benzene.

Like ultimate organic analysis, and for similar

\* *Chem News*, xxxviii. 300.

reasons, the determination of vapour densities is more frequently of service in original organic research than in the examination and assay of commercial organic products, and it is, therefore, unnecessary to refer in detail to the methods of taking vapour densities.\*

**Determination of the boiling point.**—In making this important determination, it is necessary to remember that a boiling liquid is often several degrees hotter than the vapour rising from it. In observing the boiling point, therefore, care must be taken that the thermometer bulb is not immersed in, but is situated slightly above the surface of the liquid, which should be caused to boil rapidly. In accurate determinations attention must be paid to the barometric pressure at the time, and the errors to which the thermometer is itself liable should not be neglected. Coupled with the determination of the boiling point, a partial separation of the proximate constituents is often possible. This, in the case of two or more volatile bodies having different boiling points, is the useful process known as fractional distillation. By repeating it, and collecting separately the fractions which distil at every small increase of temperature, very perfect separation may sometimes be effected. Of course the process of distillation will effect perfect separation of readily volatile and wholly non-volatile bodies. Instances of the use of the boiling point as a proof of purity will be found on pages 168, 178, and of distillation for the separation of proximate principles on pages 74, 94, 113, and 114.

**The melting point or solidifying point** of an organic body is often an important proof of its purity. Details of the method of applying the test are given on page 168.

**The determination of the crystalline form** of organic bodies is frequently of considerable value as a means of iden-

\* A very simple and convenient method of determining vapour densities has been recently described by V. Meyer (*Dent. Chem. Ges. Ber.* xi. p. 1867, and *Journ. Chem. Soc.*, 1879, ii. 177.)



tification, but is rarely a test of their purity. In the great majority of cases the crystals are too small or indistinct to admit of any goniometric determination, though the action on polarised light may frequently be observed. As a rule, the crystalline form of organic bodies is a character of inferior value. Instances to the contrary are to be found in the cases of cholesterin, salicylic acid, tartaric acid, &c.

**The optical characters** of organic bodies are often very peculiar, and of great service for identification, and even for determination. In addition to the well-known phenomena of polarised light dependent on crystalline form, many substances which are not actually crystallised exhibit a cross and series of rings when viewed by polarised light. This is notably the case with certain of the starches, and furnishes a valuable means for their discrimination.

Many organic substances possess the power of rotating the plane of polarisation of a luminous ray; and, as this property is exerted even by solutions of active substances, the angle through which the rotation occurs often serves for the accurate determination of certain bodies. The method is employed for the assay of sugar and its solutions, and in some other cases.

The specific rotatory power of a substance is found by dividing the angle of rotation observed in the polariscope ( $\alpha$ ), by the length of the column of liquid in decimetres ( $l$ ), by the weight of the active substance in each unit of liquid ( $w$ ), and by the density of the solution ( $d$ ). Thus, if  $S$  represent the specific rotatory power, then

$$S = \frac{\alpha}{l \times w \times d}.$$

For example, a solution containing .155 grammes of cane sugar in 1 gramme of solution of 1.06 specific gravity,\* rotates the

\* In practice it is convenient to weigh out a certain amount of the substance, dissolve it in water or other suitable solvent, and then make up the liquid to a known volume. When this course is taken, for  $w \times d$  is substituted  $v$ , the weight of active substance in 1 c.c. of the liquid. This, in the sample given, would be  $w \times d = v = .1643$ .

plane of polarisation through an angle of  $24^\circ$ , in a column 2 decimetres in length. Therefore

$$S = \frac{24}{2 \times .155 \times 1.06} = 73.$$

Hence  $73^\circ$  is the specific rotatory power of cane sugar.

TABLE OF SPECIFIC REFRACTIVE POWERS OF ACTIVE ORGANIC BODIES.

Active Substance in Solution.	Nature of Solvent.	Formula of Active Substance.	Refrangibility of Light.	Specific Rotatory Power.
Amygdalin . . .	Water	$C_{20}H_{27}NO_{11}$	Y	- 35.5
Camphoric Acid . . .	"	$C_{10}H_{16}O_4$	T	$\pm 38.9$
Camphor . . .	Alcohol	$C_{10}H_{16}O$	T	$\pm 47.4$
Cholesterin . . .	"	$C_{26}H_{44}O$	D	- 31.59
Glycocholic Acid . . .	"	$C_{26}H_{43}NO_6$	D	+ 29
Hematoxylin . . .	...	$C_{16}H_{14}O_6$	Y	+ 92
Malic Acid . . .	Water	$C_4H_6O_5$	T	- 50
Santonin . . .	Alcohol	$C_{15}H_{18}O_3$	T	- 230 at $20^\circ C.$
Tartramide . . .	...	$C_4H_8N_2O_4$	Y	$\pm 133.9$
Tartaric Acid . . .	Water	$C_4H_6O_6$	Y	$\pm 9.6$
Tart. Ammonium (neutral)	"	$C_4H_8O_6(NH_4)_2$	Y	$\pm 29$
Taurocholic Acid . . .	...	$C_{26}H_{45}NSO_7$	Y	+ 25.3
Egg Albumin . . .	Water	...	D	- 35.5
Serum Albumin . . .	"	...	D	- 56
Coagulated Albumin . . .	Potassa	...	D	- 58.5
Casein . . .	"	...	D	- 91
Cinchonine . . .	Alcohol and HCl	$C_{20}H_{24}N_2O$	T	- 190.4
Morphine . . .	"	$C_{17}H_{19}NO_3$	R	- 88.04
Narcotine . . .	"	$C_{22}H_{23}NO_7$	T	- 130
Quinidine . . .	"	$C_{20}H_{24}N_2O_2$	T	+ 250.75
Quinine Sulphate . . .	Acidulated Water	$2C_{20}H_{24}N_2O_2, H_2SO_4$	R	- 147.74
Strychnine . . .	"	$C_{21}H_{22}N_2O_2$	R	- 132.07
Amylic Alcohol . . .	...	$C_5H_{12}O$	D	- 4.38
Valeric Acid . . .	...	$C_5H_{10}O_2$	D	+ 4.2
Cane Sugar (Sucrose) . . .	Water	$C_{12}H_{22}O_{11}$	T	+ 73.8
Milk Sugar (Lactose) . . .	"	$C_{12}H_{22}O_{11}$	T	+ 59.3
Glucose, Dextrose* . . .	"	$C_6H_{12}O_6$	T	+ 56
" Levulose . . .	"	$C_6H_{12}O_6$	T	{ - 106 at $14^\circ C.$ - 53 at $90^\circ C.$
" Galactose . . .	"	$C_6H_{12}O_6$	T	+ 83.3
" Maltose . . .	"	$C_6H_{12}O_6$	T	+ 168
" Inverted Sugar . . .	"	$2C_6H_{12}O_6$	T	{ - 25 at $15^\circ C.$ - 12.5 at $25^\circ C.$
Dextrin . . .	"	$C_6H_{10}O_5$	T	+ 138.7

\* According to Hoppe-Seyler, the true rotatory power for pure dextro-glucose prepared from diabetic urine is  $53.5^\circ$ . He attributes the difference between this and the accepted value for glucose obtained from other sources to the invariable presence of dextrin or other impurities in all but diabetic dextrose.

As the rotatory power varies somewhat with the refrangibility of the ray of light employed for the experiment, and with the temperature of the liquid, these conditions should not be neglected.

In the preceding table are given the specific rotatory powers for some of the most important active organic substances. The letters in the fourth column refer to the refrangibility of the light employed; Y signifies the mean yellow, and R the mean red ray. D is the sodium ray, and T the "*teinte du passage*," or "transition tint." The values for T correspond with those for Y, and the values for the red ray may be obtained from them by multiplying the rotatory power by the factor .767.

THE ABSORPTION SPECTRUM of an organic substance occasionally furnishes information not to be obtained in any other way. Of course, it only gives indications with coloured substances. In the examination of blood stains, of dyeing matters, and of the colouring matters of wine, the observation of the absorption spectrum is often of great importance.

The method of applying the test requires no special description at present.

### 3. EXAMINATION OF THE SOLUBILITY IN VARIOUS MENSTRUUA.

The distinction and separation of bodies by their different degrees of solubility in water, acid, &c., is a method of chemical examination with which the merest tyro is familiar. There is, however, one method of applying a solvent, which is little used in mineral analysis, but which is often extremely useful in the separation of proximate organic principles. It consists in shaking the liquid to be examined with some other liquid with which it is incompletely miscible. Thus, if an aqueous solution of a substance very soluble in ether, chloroform, or benzene be shaken with one of those liquids, it will be removed more or less completely from its aqueous solution, and on repeatedly treating the aqueous liquid with a fresh portion of





Indigotin	$C_{16}H_5NO_2$	288	...	I	I	I	I	I	I	I	I	...	I	...	...	I	...	Soluble in hot phenol and creasote, and in strong sulphuric acid. Sparingly soluble in cold spirit, ether, or benzene.
Naphthalene	$C_{10}H_8$	218	79.2	I	I	I	I	I	I	I	I	S	...	...	...	S	...	Slightly soluble in hot water. Slightly soluble in water. Alkaline solutions red.
Anthracene	$C_{14}H_{10}$	260	212	I	I	I	I	I	I	I	I	S	...	...	...	S	...	Soluble in hot spirit, insoluble in cold.
Alizarin	$C_{14}H_8O_4$	275	275	I	(1)	I	S	...	...	...	...	S	I	...	...	I	...	Slightly soluble in hot water. Slightly soluble in water. Alkaline solutions red.
Aurin	$C_{19}H_{14}O_3$	...	...	I	I	I	I	I	I	I	I	(S)	...	...	...	S	...	Soluble in hot spirit, insoluble in cold.
Paraffin Wax	$CnH_{2n+2}$	45-65	370	I	I	I	I	I	I	I	I	...	...	...	...	...	...	Slightly soluble in hot water. Slightly soluble in water. Alkaline solutions red.
Oil of Turpentine	$C_{10}H_{16}$	161	...	I	I	I	I	I	I	I	I	...	...	...	...	...	...	Soluble in hot spirit, insoluble in cold.
Cane Sugar	$C_{12}H_{22}O_{11}$	160	...	300	I	I	I	I	I	I	I	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Grape Sugar	$C_{12}H_{22}O_{11}$	70	...	100	I	I	I	I	I	I	I	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Milk Sugar	$C_{12}H_{22}O_{11}$	...	...	20	40	S	S	S	S	S	(1)	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Mannite	$C_6H_{14}O_6$	165	...	16	S	S	S	S	S	S	(1)	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Indefinite	Indefinite	...	...	S	S	S	S	S	S	S	...	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Starch	$C_6H_{10}O_5$	...	...	I	I	I	I	I	I	I	I	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Dextrin	$C_6H_{10}O_5$	...	...	S	S	S	S	S	S	S	...	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Gum Arabic (Arabin)	$C_{12}H_{22}O_{11}$	...	...	S	S	S	S	S	S	S	...	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Acetic Acid	$C_2H_4O_2$	119	16.7	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Slightly soluble in rectified spirit. Soluble in spirit to extent of 40%.
Oxalic Acid (crystallised)	$C_2H_2O_4 \cdot 2H_2O$	Subl. 157	...	8	350	S	S	S	S	S	15	...	...	...	...	I	...	Soluble in ether to extent of 14%.
Lactic Acid	$C_3H_6O_3$	125	180	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Soluble in 13 parts of absolute alcohol. Decomposed on boiling.
Succinic Acid	$C_4H_6O_4$	(235)	...	8	60	S	S	S	S	S	12½	...	...	...	...	...	...	Soluble in ether to extent of 4%. Decomposed by fusion.
Malic Acid	$C_4H_6O_5$	...	...	S	S	S	S	S	S	S	...	...	...	...	...	...	...	Soluble in ether to extent of 14%.
Tartaric Acid	$C_4H_6O_6$	(170)	...	25	100	S	S	S	S	S	41	...	...	...	...	...	...	Soluble in 13 parts of absolute alcohol. Decomposed on boiling.
Racemic Acid	$C_4H_6O_6$	...	...	20	...	S	S	S	S	S	...	...	...	...	...	...	...	Soluble in ether to extent of 4%. Decomposed by fusion.
Citric Acid	$C_6H_8O_7 \cdot H_2O$	...	...	133	200	S	S	S	S	S	53	...	...	...	...	...	...	Absolute alcohol dissolves 39%. Soluble in about 150 parts of ether.
Meconic Acid	$C_8H_8O_7 \cdot 3H_2O$	...	...	9	S	S	S	S	S	S	12	...	...	...	...	...	...	Decomposed by heat. Very soluble in absolute alcohol.
Galic Acid	$C_7H_6O_5 \cdot H_2O$	222-240	...	I	33	S	S	S	S	S	23	...	...	...	...	...	...	Solution in soda turns rapidly brown in air.
Pyrogallallic Acid	$C_3H_6O_3$	131	...	33	S	S	S	S	S	S	...	...	...	...	...	...	...	Decomposed on boiling.
Gallo-tannic Acid	Indefinite	...	...	S	S	S	S	S	S	S	...	...	...	...	...	...	...	Slightly soluble in cold water.
Sulphonaphenic Acid	$C_6H_6SO_4$	...	...	I	S	S	S	S	S	S	...	...	...	...	...	...	...	Alkaline solution is purple-red.
Picric Acid	$C_6H_3N_3O_7$	122	...	1	8	S	S	S	S	S	...	...	...	...	...	...	...	Very slightly sol. in cold water.
Benzoic Acid	$C_7H_6O_2$	120	249	1	1	S	S	S	S	S	42	...	...	...	...	...	...	Alkaline solution is purple-red.
Hippuric Acid	$C_9H_9NO_3$	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Salicylic Acid	$C_7H_6O_3$	125	(200)	(1)	S	S	S	S	S	S	...	...	...	...	...	...	...	...
Phthalic Acid	$C_8H_6O_4$	182	...	I	S	S	S	S	S	S	...	...	...	...	...	...	...	...
Chrysophanic Acid	$C_{15}H_{10}O_4$	162	...	I	(1)	I	...	...	...	...	...	...	...	...	...	...	...	...



the solvent, a very complete separation can frequently be effected. Sometimes the reverse course is taken, and a substance readily soluble in water is removed from the sample by agitating it with water or an aqueous liquid. Such a plan is used for separating alcohol from chloroform or ether, carbonic acid from coal oils, &c. In some cases a graduated tube can be conveniently employed, and the change in the volume of the sample read off after complete separation of the two liquids.

The foregoing table (pp. 12, 13) gives the solubilities in various menstrua of a number of organic substances. Alkaloids and glucosides are purposely omitted, as they will require treatment in a separate table. The same is true of the various oils, fats, and essential oils. When not otherwise stated the solubilities are supposed to refer to the use of the solvents at ordinary temperatures. A separate column has been added showing the solubility in boiling water.

In the table, S signifies soluble, and I insoluble. When the letter is placed within parenthesis, the substance cannot be strictly classified in either way, and some remark on the subject will generally be found in the last column. The sign  $\infty$  indicates that the substance is infinitely soluble or miscible with the solvent in all proportions.

The data from which the table is compiled have been obtained from the best available sources, but curious discrepancies exist in the statements on record respecting the solubility of organic bodies, and hence the accuracy of the statements in the table cannot in all cases be guaranteed.

To render the table more complete, there have been added columns showing the formulæ, densities, and boiling and melting points of the substances referred to. The densities are in many cases merely approximate, owing to the varying conditions under which they were observed. The same remark applies with less force to the boiling and melting points.

#### 4. ULTIMATE or ELEMENTARY ANALYSIS.

When organic substances are heated to redness in the air or in presence of oxygen-yielding substances, they are generally completely oxidised, the carbon being burnt to carbonic dioxide, and the hydrogen to water. Nitrogen is evolved for the most part in the free state, but in some cases partly in combination with oxygen. Sulphur and phosphorus are also converted into oxides, and the same with such of the metals as combine with oxygen at a red heat. A few substances, such as potassium cyanate, resist the action of dry air at a red heat. Substances containing the metals of the alkalis or alkaline earths in the form of salts of organic acids, leave these metals in the form of carbonates;\* hence the carbon dioxide evolved in the form of gas will be less than that corresponding to the total carbon present.

Although an elementary analysis is frequently the most satisfactory mode of establishing the composition and even the identity of an organic substance, it is subject to grave disadvantages. Thus, as it merely determines the total amount of the elements present, it affords no clue to the arrangement of the atoms, and in many cases does not even give the number of atoms of each element present. Thus the percentage of carbon and hydrogen in an organic substance having been duly determined, there would still be no indication which of the individual members of the particular group of bodies it might represent.

For example: suppose that a substance when analysed has been found to contain

$$C = 85.74 \text{ per cent.}$$

$$H = 14.28 \quad ,,$$

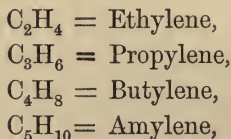
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$$100.00$$

Dividing in each case the respective percentages of carbon and hydrogen by their atomic weights, we arrive at  $CH_2$ , as

\* In a few instances other salts may be left. Thus, sodium sulphophenate leaves sodium sulphate on ignition.

the simplest possible representation of the substance analysed. But this is the general expression for the large group of hydrocarbons called olefines, and the method is quite incompetent to tell us whether the substance examined really consisted of

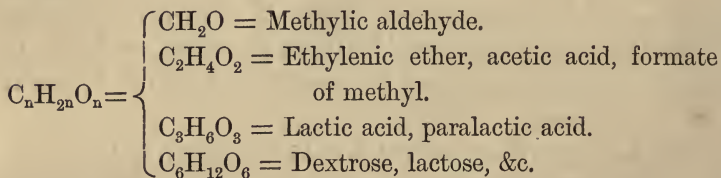


or of any other member of the same homologous series expressed by the general formula  $\text{C}_n\text{H}_{2n}$ .

Again, suppose the substance was found by analysis to have the following composition—

$$\begin{array}{rcl} \text{C} & = & 40\cdot00 \text{ per cent.} \\ \text{H} & = & 7\cdot27 \quad \text{,,} \\ \text{O} & = & 52\cdot73 \quad \text{,,} \\ \hline & & 100\cdot00 \end{array}$$

These figures correspond to the empirical formula  $\text{CH}_2\text{O}$ , or a multiple of this, and from the results of the elementary analysis *alone*, it might still be any one of the following bodies.



Another serious difficulty which affects ultimate organic analysis is the necessity for extreme purity of the substance analysed, as a mixture of two bodies will give figures which baffle all attempts at interpretation. On the other hand it might be supposed that the fact that an elementary analysis yielded figures closely in accordance with theory was in itself a guarantee of the purity of the body analysed. This, however,

is by no means universally the case. In the first place, small proportions of foreign matter altogether escape detection, and in special cases as much as 10 per cent. or more of a common impurity will scarcely show itself in the percentages of carbon and hydrogen obtained. Thus the presence of 10 per cent. of common alcohol in ethyl acetate would cause a difference in the percentage of carbon of but 0.23 per cent., and of hydrogen 0.40 per cent. Similarly, 10 per cent. of amylic alcohol in amyl acetate would cause a variation of but 0.37 per cent. in the carbon, and 0.28 per cent. in the hydrogen.

Hence the value of elementary analysis as a means of chemically examining and assaying commercial organic products is comparatively limited, though for the purposes of original organic research it is simply irreplaceable. As this work is intended more for use in the commercial laboratory than for employment by the student in search of new organic bodies, and as every text-book already published contains a description of the ordinary methods of making an organic combustion, it is unnecessary to give the details here, and to describe the methods at any length without working details would merely be waste of space.

The following general outlines may, however, be found of service in enabling a suitable method of analysis to be chosen.

**Carbon and Hydrogen** are determined by igniting the substance with dry oxide of copper, with or without the assistance of a stream of oxygen or purified air.\* The resultant water is absorbed by sulphuric acid or dry calcium chloride, and the carbon dioxide by caustic potash solution or soda-lime. In presence of sulphur, chlorine, bromine, iodine, or light metals, chromate of lead is substituted for the cupric oxide. Mercury is liable to distil over into the water absorption apparatus. In presence

\* F. Kopfer has recently described an apparently excellent method of organic analysis by burning the substance in oxygen, and passing the products of combustion over metallic platinum (*Journ. Chem. Soc.* xxix. 660). Dupré has described a plan of determining very small quantities of carbon (*Journ. Chem. Soc.* xxxv. p. 159).



of nitrogen the anterior part of the tube is filled with metallic copper, or, far preferably, silver, to reduce any oxides of nitrogen. Silver also retains chlorine, &c.

**Nitrogen** may be detected by heating the substance (if a liquid, absorbed by asbestos or sand) with metallic sodium in a narrow test-tube. Cyanide is formed, which may be dissolved out with cold water, and detected by tests 3 and 4, page 29.

Most compounds containing nitrogen give off the whole of it as ammonia on ignition with soda-lime. Some, such as indigo, yield volatile organic bases instead. These all resemble ammonia in the fact that their hydrochlorates form double salts with platinic chloride, which when ignited leave 100 parts of Pt. for 14.2 of N.

NITRO-SUBSTITUTION COMPOUNDS, such as picric acid, do not evolve the whole of the contained nitrogen as ammonia when ignited with soda-lime. Addition of sugar improves the result.

CYANOGEN COMPOUNDS may be ignited with soda-lime if a high temperature be employed. Admixture with sugar is desirable.

A general process for determination of nitrogen is combustion with oxide of copper (passing gaseous products over red-hot metallic copper or silver), absorption of carbonic acid by solution of potash, and measurement of residual gaseous nitrogen.

**Chlorine, Bromine, and Iodine\*** may be detected by igniting in a stream of hydrogen, and passing the gas into nitrate of silver. They are best determined by ignition with excess of pure quick-lime and pounded glass, with subsequent conversion into silver-salts. Another good method is based on ignition with ferric oxide, with subsequent conversion to silver salts.

**Sulphur, Phosphorus, and Arsenic†** may be detected

\* *Journ. Chem. Soc.* xxix. 961, and xxxii. 225.

† A comprehensive and apparently accurate method for determining these elements has been recently described by Brügelmann (*Zeitsch. Anal. Chem.* xvi. 1, and *Journ. Chem. Soc.* xxxi. 739).

by igniting the substance with pure soda-lime mixed with an oxidising agent, such as nitre, chlorate of potassium, or mercuric oxide. The residue is tested for sulphates, phosphates and arseniates. The process may be made quantitative. Another method is to heat the substance in a sealed tube with nitric acid of 1.2 sp. gr. The sulphur, phosphorus and arsenic are converted respectively into sulphuric, phosphoric and arsenic acids.

**Metals** usually remain in the residue left on igniting the organic substance in the air. Metals of the alkalis and alkaline earths are usually left as carbonates, but sometimes more or less completely as sulphates, phosphates chlorides, &c. Heavy metals are usually left as oxides, except silver, gold, and platinum, which will remain in the free state. Arsenic, antimony, and other metals when existing in volatile compounds may be completely volatilised.

MERCURY will be wholly volatilised. It may be determined in all instances by igniting the substance with soda-lime, and collecting and weighing the mercury which distils over.

**Oxygen** may be detected in organic bodies containing it by ignition in a stream of hydrogen, when water will be formed. By igniting the substance in a stream of chlorine, or in admixture with potassium chloroplatinate, carbon dioxide will be formed if oxygen be present. Hydrochloric acid and chlorine may be respectively absorbed by solutions of lead nitrate and stannous chloride, and the carbonic acid passed into solution of potash or baryta-water.

In the great majority of instances the oxygen of organic bodies is determined by difference.

## PRODUCTION OF DEFINITE COMPOUNDS, AND STUDY OF PRODUCTS OF DECOMPOSITION OF ORGANIC BODIES.

These modes of research are too well known to every student of chemistry to require special description, the great

majority of the methods of quantitative analysis, both gravimetric and volumetric, being based on these principles.

**Normal Solutions.**—In employing standard solutions for volumetric determinations, the terms “normal,” “decinormal,” &c., are employed in this work in the same signification in which they are used by Sutton. Thus, a normal solution is one containing in 1000 cubic centimetres such an amount of the active constituent as will combine with, replace, or oxidise 1 gramme of hydrogen. Hence normal and decinormal solutions of the following substances have the strengths given below.

		Grammes per litre.
Normal Caustic Soda	contains Na	= 23
” ” ”	” NaHO	= 40
” ” Potash	” KHO	= 56·1
” Carbonate of Sodium	” $\frac{\text{Na}_2\text{CO}_3}{2}$	= 53
Decinormal Lime Water	” $\frac{\text{CaO}}{20}$	= 2·8
” Baryta Water	” $\frac{\text{BaO}}{20}$	= 7·65
Normal Hydrochloric Acid	” HCl	= 36·5
” Sulphuric Acid	” $\frac{\text{H}_2\text{SO}_4}{2}$	= 49
” Oxalic Acid	” $\frac{\text{C}_2\text{H}_2\text{O}_4, 2\text{H}_2\text{O}}{2}$	= 63
Decinormal Silver Nitrate	” $\frac{\text{AgNO}_3}{10}$	= 17·0
” Mercuric Chloride	” $\frac{\text{HgCl}_2}{20}$	= 13·55
” Potassium Permanganate	” $\frac{\text{KMnO}_4}{50}$	= 3·162

## CYANOGEN AND ITS DERIVATIVES.

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ORGANIC CHEMISTRY has been called the "Chemistry of Compound Radicals." One of the most remarkable and best known of compound radicals is the substance *Cyanogen*, which is not only obtainable in a free state, but enters into direct combination with the metals, forms an acid with hydrogen, and a well-defined series of salts called cyanides. It also forms an oxy-acid and thio-acid, each of which has its own series of salts. Cyanogen presents greater analogies to iodine than to any other element, but has special chemical peculiarities which are without parallel in the case of any other radical, either simple or compound.

Cyanogen is composed of carbon and hydrogen united in atomic proportions. Hence its formula is CN, or in the free state  $C_2N_2$ . Cyanogen is very often expressed by the symbol Cy.

All bodies containing cyanogen in whatever form, yield, when strongly ignited with excess of soda-lime, the whole of their nitrogen in the form of ammonia.

The analytical reactions of cyanogen compounds and derivatives will be considered under their respective heads.

### **CYANOGEN GAS.** $C_2N_2 = Cy_2$ .

This gas is not often met with in a free state except when purposely produced by heating mercuric or argentic cyanide. It is a heavy colourless gas, smelling at once of bitter-almonds and chlorine, and burning when kindled with a rose-coloured flame. It is readily soluble in water and alcohol, and is very



poisonous. When exploded with oxygen in the endiometer cyanogen yields carbon dioxide and nitrogen.

Cyanogen is one of the products of the dry distillation of ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 4\text{H}_2\text{O} + 2\text{CN}$ ), and is sometimes present in crude coal gas and in waste gases from blast furnaces. It may be detected by passing the gases through solution of caustic alkali, when the cyanogen is absorbed with production of a cyanide and cyanate ( $2\text{CN} + 2\text{KHO} = \text{H}_2\text{O} + \text{KCN} + \text{KCNO}$ ). The cyanide can then be detected by the reactions described on pages 28 and 29.

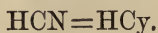
**Paracyanogen**,  $\text{C}_n\text{N}_n$ , is the name given to a brown amorphous solid frequently produced in the preparation of cyanogen gas, and formed by the spontaneous decomposition of hydrocyanic acid. When heated in a current of nitrogen or carbonic dioxide it is gradually volatilised as cyanogen gas, which may be absorbed by solution of caustic alkali.

## HYDROCYANIC ACID.

### Hydrogen Cyanide—Prussic Acid.

*French*—Acide Cyanhydrique.

*German*—Blausäure.



ANHYDROUS HYDROCYANIC ACID is an intensely poisonous, unstable, very volatile liquid, produced by passing sulphuretted hydrogen over mercuric cyanide. ( $\text{HgCy}_2 + \text{H}_2\text{S} = \text{HgS} + 2\text{HCy}$ .)

DILUTE HYDROUS HYDROCYANIC ACID is prepared by distilling potassium ferrocyanide with dilute sulphuric acid ( $2\text{K}_4\text{FeCy}_6 + 6\text{H}_2\text{SO}_4 = \text{Fe}''\text{K}_2\text{FeCy}_6 + 6\text{KHSO}_4 + 6\text{HCy}$ .) Dilute hydrocyanic acid is a colourless and very volatile liquid. It has a peculiar bitter taste and almond-like odour. It reddens litmus paper slightly. The acid of the "British Pharmacopœia" is supposed to contain 2 per cent. of real  $\text{HCy}$ , but even this dilute acid is very liable to change, turning brown

and producing paracyanogen, formic acid, and other products. The formation of urea has been observed. Sometimes a solid mass results. Samples containing traces of mineral acids are said to keep better than perfectly pure specimens, but the truth of this statement is doubtful.\* Woodman and Tidy found sixteen samples, sold in one neighbourhood as the B. P. acid, to contain amounts of real HCN varying from 0·6 to 3·2 per cent., and other observers have not unfrequently met with commercial specimens containing as little as ·25 per cent.

The following table shows the normal strength of various official qualities of hydrocyanic acid:—

Pharmacopœia.	HCN.
America . . . . .	2·0 per cent.
Austria . . . . .	2·5 „
Baden . . . . .	2·5 „
Batavia . . . . .	2·5 „
Bavaria . . . . .	4·0 „
Borussia (6th edition) . . . . .	2·0 „
British . . . . .	2·0 „
(London . . . . .	2·0) „
(Edinburgh . . . . .	3·3) „
(Dublin . . . . .	3·3) „
France . . . . .	10·5 „
Hessia . . . . .	18· to 20· „
Norway* . . . . .	2·0 „
Saxony . . . . .	1·9 „
Switzerland . . . . .	2·0 „
Scheele's Acid . . . . .	5·0 (?) „
Vauquelin's Acid . . . . .	3·5 „

Very weak hydrocyanic acid (containing ·1 or ·2 per cent. of HCN) is much more permanent than the stronger kinds, and can be kept with practically little change. Mr J. Williams has observed that hydrocyanic acid, even when of considerable strength, can be kept fairly well if 20 per cent. of glycerin be added to it; thus a sample containing  $37\frac{1}{2}$  per cent. of HCN,  $37\frac{1}{2}$  of water, and 25 per cent. of glycerin kept without change for a period of four years.

The best way of extemporising hydrocyanic acid of known

\* The acid of the Norwegian Pharmacopœia receives an addition of 0·1 per cent. of strong sulphuric acid.

strength is to agitate cyanide of silver with an equivalent amount of dilute hydrochloric acid. The hydrocyanic acid of the French Pharmacopœia is prepared in this way. Another very convenient plan is to decompose cyanide of potassium, or the double cyanide of potassium and zinc (a very stable salt), with tartaric acid. Twenty-two grains of the double cyanide,  $K_2ZnCy_4$ , and 49 grains of tartaric acid dissolved in 1 ounce of water, give, on filtration or decantation from the precipitate, a liquid containing 2 per cent. of HCN.

The strength of free hydrocyanic acid and of liquids containing it is readily ascertained by gravimetric precipitation with nitrate of silver, or by volumetric estimation by Liebig's or Hannay's process. (See page 32, *et seq.*)

The qualitative tests for hydrocyanic acid are described on pages 28 and 29.

The impurities present in commercial hydrocyanic acid are due to its mode of preparation, or its subsequent decomposition, and are generally of but little importance.

In every form, to every animal, and however administered, prussic acid is an intensely active *poison*. Swallowed, injected, inhaled, and sometimes even when merely applied to the sound skin, its action is energetic. An internal dose of three or four grains of real hydrocyanic acid is generally fatal to the human subject, and less than one grain has been known to cause death.

To the presence of hydrocyanic acid the poisonous properties of the essence of cherry kernels, bitter-almond water (and the crude oil), and laurel water are due. Good *Kirshwasser* sometimes contains upwards of 1 grain of prussic acid to the pint, and inferior specimens often four times as much.

Prussic acid does not appear to exist ready-formed in the plants yielding it, but to be produced by the action of a peculiar ferment on the glucoside amygdalin,  $C_{20}H_{27}NO_{11}$ , which, under its influence and in presence of water, splits up with formation of glucose, benzoic aldehyde, and hydrocyanic acid. (See "Benzoic Aldehyde.")

Theoretically, 100 parts of amygdalin should yield 5·91 of prussic acid, and the practical results are not far removed from this proportion. The following are the usual proportions of amygdalin contained in, and of prussic acid obtainable from various natural sources :\*—

	Contains Amygdalin.	Yields HCN.
Bitter-almond Pulp . . .	4½ per cent.	·25 per cent.
Cherry-stone Kernels . . .	3 "	·17 "
Wild Service Kernels . . .	1½ "	·08 "
" Flower, Root, and Bark	1 "	·06 "
Sweet Cassava Root . . .	·3 "	·017 "
Bitter " . . .	·45 "	·027 "

The following are the usual proportions of hydrocyanic acid present in certain preparations containing it:—

	HCN.
+ Crude Bitter-almond Oil . . .	8 to 15 per cent.
+ Bitter-almond Water . . .	¼ to 1 "
Cherry Laurel Oil . . .	2 to 3 "
+ " Water . . .	¼ to ¾ "
Cluster Cherry Oil . . .	9 to 10 "

In the case of all these liquids, the proportion of hydrocyanic acid, and, consequently, the poisonous effects become greatly diminished by long keeping. The oils may be assayed for hydrocyanic acid by the methods described under "benzoic aldehyde," and the aqueous liquids as described on p. 31, *et seq.*

**The Toxicological Detection of Hydrocyanic Acid** is rendered difficult by its great tendency to decompose. Hence, detection in the body is rarely possible more than twenty-four hours after death.

\* Although in medico-legal investigations the possible introduction of hydrocyanic acid into the body from natural sources should not be overlooked, the importance of such sources of error is generally much overrated. This is well illustrated in the following case:—An expert was pressed, in the witness box, to say whether apple-pips did not contain prussic acid, and, if so, whether the fact of their having been found in the stomach of the deceased might not account for his death. After professing his inability to state the exact amount of prussic acid obtainable from apple-pips, and being encouraged to express his opinion as to the quantity of pips requisite to yield a fatal dose of the poison, he caused the collapse of the defence by opining that "about a peck" might suffice.

† For further information on these products, see "benzoic aldehyde."



On opening the stomach and intestines the odour of the acid is often perceptible. These viscera are often quite natural in appearance, but sometimes more or less inflamed and congested. The lungs, liver, spleen, and kidneys are always found gorged with blood. The venous system is invariably gorged with blood, the arteries being empty. The blood has undergone change; it may be black or oily, or of a cochineal red colour. It often smells of the poison, which may frequently be distilled from it.

To detect hydrocyanic acid in the contents of a stomach the analyst should proceed as follows:—

Note the reaction of the liquid portion. If not distinctly alkaline, the poison (if present) was probably administered as free hydrocyanic acid, and not as cyanide of potassium. (The various double cyanides used for electro-deposition of metals have a neutral reaction in the absence of excess of potassium cyanide.)

Stir up the stomach and its contents with cold water, and introduce the thick liquid into a flask adapted to a Liebig's condenser, allowing the end of the condensing tube to be immersed in a small quantity of water. Apply a moderate heat to the flask (best by an external bath of salt water), and distil over about half the liquid. To the distillate apply carefully tests 2, 3, and 4 on pages 28 and 29. It is preferable to avoid any addition of acid to the liquid to be examined, as the saliva contains traces of thiocyanates (sulphocyanides), which might possibly give traces of hydrocyanic acid on distillation with a mineral acid. If the distillate has given negative results when tested for prussic acid, continue the distillation after rendering the contents of the flask distinctly acid with tartaric acid. If hydrocyanic acid be now found in the distillate, the poison must have been present as a readily decomposable cyanide. Before finally concluding that metallic cyanides are absent, it is desirable to repeat the distillation after adding a considerable excess of moderately dilute sulphuric and hydro-

chloric acids. Ferro- and ferri-cyanides and cyanide of mercury will in this case be decomposed. The absence of ready-formed ferro- and ferri-cyanides should be ascertained by testing a portion of the acidulated contents of the stomach with solutions of ferric and ferrous salts.\*

If only a small quantity of hydrocyanic acid be present in the distillate, it is most conveniently detected by concentrating it in the form of cyanide of silver by precipitating the liquid with nitrate of silver, and then applying the iron and sulphur tests to portions of the precipitate.

One of the causes for the disappearance of hydrocyanic acid in the dead body in its reaction with the sulphide of ammonium produced by putrefaction, whereby sulphocyanides (thiocyanates) are formed. Therefore, in the case of a body which has been dead a considerable time, hydrocyanic acid may sometimes be detected by rendering the materials distinctly, but not excessively, alkaline with caustic potash, and then adding excess of alcohol. The liquid is filtered, and evaporated to dryness. The residue is redissolved in water, acidulated with hydrochloric acid, and ferric chloride added, when a red colour will be produced if a thiocyanate were present in the stomach.

A mixture of solution of ferrous sulphate and alkali is sometimes given as an antidote in cases of poisoning by prussic acid. On acidulating the contents of the stomach with hydrochloric acid, Prussian blue will be formed if hydrocyanic acid had been taken.

## **METALLIC CYANIDES.**

Cyanogen forms a series of very well defined salts called Cyanides, having a remarkable tendency to form compounds with each other, which are often of an exceedingly stable character. Hence the properties of these double cyanides are

\* Ferrocyanides are not poisonous, unless they contain a poisonous metal.

often much modified and many of them do not respond to the tests for simple cyanides and hydrocyanic acid.

**Simple Cyanides.**—On ignition *per se* cyanides of the noble metals yield the metal, cyanogen gas, and more or less paracyanogen,  $Cy_n$  (see page 22); the cyanides of iron are decomposed into carbide of iron and free nitrogen; cyanides of the alkali-metals are not affected by simple ignition in the absence of air, but in the presence of oxygen they are converted into the corresponding cyanates, and in presence of vapour of water yield more or less ammonia and leave an alkaline carbonate.

Heated with potassium nitrate or chlorate, cyanides detonate strongly.

The cyanides of the alkali- and alkaline-earth-metals are soluble in water, the former readily, the latter with difficulty. They are decomposed by atmospheric carbonic acid with liberation of hydrocyanic acid.

The cyanides of the heavy metals are insoluble in water, with the exception of mercuric and thallium cyanides (see p. 39).

A solution of the cyanide of potassium or other light metal gives the following reactions:—

1. On warming with dilute hydrochloric acid, poisonous hydrocyanic acid is evolved, smelling of bitter-almonds.

2. Argentic nitrate, added in excess, throws down white curdy argentic cyanide ( $AgCy$ ), exactly resembling the corresponding chloride in appearance and general properties. The washed precipitate differs from the chloride:—

*a.* By evolving  $HCy$ , when boiled with hydrochloric acid.

*b.* By dissolving in concentrated nitric acid ( $AgCl$  is insoluble), yielding a solution in which silver may be detected by adding hydrochloric acid. This reaction serves to separate chloride of silver from the cyanide.

*c.* By evolving cyanogen gas on ignition, leaving metallic silver. ( $AgCl$  fuses without decomposition.)

*d.* By responding to reactions 3 and 4.



3. On adding caustic soda and ferrous sulphate, a ferro-cyanide is formed ( $6\text{KCy} + \text{FeSO}_4 = \text{K}_2\text{SO}_4 + \text{K}_4\text{FeCy}_6$ ). On acidulating the liquid with hydrochloric acid and adding ferric chloride, a Prussian blue precipitate (or bluish-green coloration) of ferric ferrocyanide is produced. If the ferrous sulphate contains any ferric salt, the addition of ferric chloride is superfluous. This test is very delicate and characteristic. It is not applicable in presence of ferro- or ferri-cyanides.

4. On evaporation to dryness at a steam-heat, after addition of yellow ammonium sulphide, a thiocyanate (sulphocyanide) is formed. On treating the residue with water, filtering if necessary, acidulating with hydrochloric acid and adding ferric chloride, a blood-red colour is produced, due to the formation of ferric thiocyanate. The colour is distinguished from that due to an acetate, by being unaffected by dilute hydrochloric acid, and from that produced by a meconate by being readily destroyed by addition of mercuric chloride. On agitation of the liquid with ether the sulphocyanide dissolves and colours the ethereal layer red. This test can be applied to cyanide of silver. Free hydrocyanic acid or a cyanide can be detected in presence of a ferro- or ferri-cyanide or thiocyanate by mixing the suspected liquid with tartaric acid, warming it, and allowing the vapours to act on a drop of yellow sulphide of ammonium contained in a porcelain dish or watch-glass, inverted over the vessel containing the sample to be tested. After some time the cover is removed, the drop of liquid evaporated to dryness, and the residue treated as above described. This elegant and delicate test is due to Liebig.

FREE HYDROCYANIC ACID responds readily to all the above tests.

MERCURIC CYANIDE reacts peculiarly, and must be examined in a special manner.

THE CYANIDES OF ORGANIC RADICALS are of no commercial importance.

**Double Cyanides.**—Many of the cyanides of the heavy



metals combine with the cyanides of the light metals, forming soluble double salts of a very stable character. These double salts are not precipitated by alkalies or decomposed by carbonic acid, and are usually quite neutral in reaction. On ignition without access of air these double cyanides are decomposed, and the alkaline cyanide may then be dissolved out from the residual heavy metal or metallic carbide by means of water.

Many of the double cyanides are decomposed on addition of a dilute mineral acid, as in the following instance:—



The liberated hydrocyanic acid has, in such cases, no tendency to combine with the cyanide of the heavy metal.

Double cyanides, which suffer decomposition in the above manner, respond to the tests for simple cyanides (pp. 28 and 29), except that the precipitate produced by nitrate of silver in a neutral solution is not pure argentic cyanide, but a mixture of the two cyanides of the heavy metals, as in the following instance:—

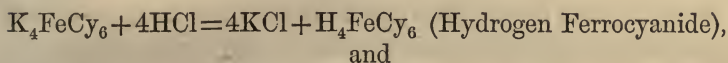


On treating the precipitate with dilute nitric acid, the cyanide of zinc dissolves and argentic cyanide remains.

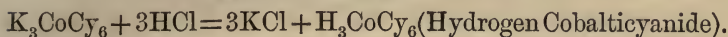
Of the readily decomposable double cyanides, those of mercury, silver, and cadmium are decomposed by sulphuretted hydrogen readily and completely, with precipitation of the corresponding metallic sulphides. Most of the other double cyanides of this class are decomposed very imperfectly, or not at all.

Other of the double cyanides are of a still more stable character, and on treatment with a dilute mineral acid, the liberated hydrocyanic acid remains in close combination with the cyanide of the heavy metal forming a new compound acid giving rise to a complete and characteristic series

of salts. The following equations represent the action of hydrochloric acid on the potassio-ferrous and potassio-cobaltic cyanides:—



and



In these cyanides neither the cyanogen nor the heavy metal is recognisable by any reaction which does not involve actual destruction of the compound cyanide.

The following are the chief classes of stable double cyanides; the more important are considered analytically in separate sections. (See page 42, *et seq.*)

Ferrocyanides	. $4\text{MCy}, \text{FeCy}_2 = \text{M}_4, \text{FeCy}_6 = \text{M}_4, \text{Cfy}'''$ .
Ferricyanides	. $3\text{MCy}, \text{FeCy}_3 = \text{M}_3, \text{FeCy}_6 = \text{M}_3, \text{Cfy}'''$ .
Nitro-ferricyanides (Nitroprussides)	$\left. \begin{array}{l} \\ \end{array} \right\} 2\text{MCy}, \text{FeCy}_3\text{NO} = \text{M}_2, \text{FeCy}_5\text{NO}.$
Cobalticyanides	. $3\text{MCy}, \text{CoCy}_3 = \text{M}_3, \text{CoCy}_6.$
Chromicyanides	. $3\text{MCy}, \text{CrCy}_3 = \text{M}_3, \text{CrCy}_6.$
Platinocyanides	. $2\text{MCy}, \text{PtCy}_2 = \text{M}_2, \text{PtCy}_4.$

**1. The Determination of Cyanogen** in free hydrocyanic acid and cyanides of the light metals may be effected by treating the solid substance or the liquid with excess of nitrate of silver solution, adding water, and then a slight excess of nitric acid. Allow the precipitated cyanide of silver to settle without applying heat; then filter, wash, and dry at  $100^\circ \text{C}$ , and weigh as  $\text{AgCy}$ , or ignite the precipitate for a considerable time in an open porcelain crucible, and weigh the residual metallic silver. 108 parts of  $\text{Ag}$ , or 134 of  $\text{AgCy}$ , represent 26 of  $\text{Cy}$ , or 27 of  $\text{HCy}$ .

BITTER-ALMOND AND CHERRY-LAUREL WATER contain cyanide of ammonium and hydrocyanate of benzaldehyde in addition to free hydrocyanic acid. To apply the process to the estimation of the total cyanogen in such liquids, after adding excess of

nitrate of silver add ammonia till the liquid is strongly alkaline, and then *at once* acidify with nitric acid.\*

In presence of sulphides, these are first removed by agitating the liquid with freshly precipitated carbonate of lead, the nitrate of silver being added to the filtrate.

In presence of chloride, the silver precipitate is dried at 100° C and weighed, then just fused, reduced by treatment with zinc and dilute sulphuric acid, filtered, and chlorine determined in the filtrate by nitrate of silver. The proportion of chloride of silver corresponding thereto is deducted from the observed weight of silver precipitate, the difference being argentic cyanide. Small quantities of cyanide in a mixture with chloride are better determined by igniting the silver precipitate with soda-lime, and determining the resultant ammonia.

The double cyanides of potassium with nickel, copper, and zinc can be analysed gravimetrically by the above method, provided that the silver precipitate be digested for some time with nitrate of silver and dilute nitric acid, the action being assisted by a gentle heat.

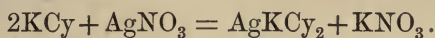
2. A very convenient and fairly accurate method of using nitrate of silver for the determination of cyanogen is that of Liebig. Some of the errors to which the process was liable have been pointed out by L. Siebold,† who has also extended the field to which the process is applicable, and has shown that it may be employed for the estimation of alkaline cyanides in presence of free hydrocyanic acid. It has also the advantage that the presence of chlorides, far from interfering, is to be preferred. Sulphides, if present, must be first removed by agitating the liquid with carbonate of lead as above described.

\* A very convenient method of assaying bitter-almond water has been recently described by Vielhaber (*Journ. Chem. Soc.* 1879, ii. 280, and *Arch. Pharm.* [3] xiii. p. 408). The liquid is shaken with hydrated magnesia till alkaline, when a few drops of acid chromate of potassium are added, and decinormal nitrate of silver run in with constant stirring, till a permanent red tint is produced. Each c.c. of decinormal  $\text{AgNO}_3$  equals '0027 grammes of HCy.

† *Pharm. Journ.* September 7, 1878, p. 191.



Formic acid and formates are without influence on the result, and the same is true of cyanates. The process is based on the fact that cyanide of silver forms a soluble double salt with cyanide of potassium, of the composition  $\text{AgCy}, \text{KCy}$ . Hence the first effect of the addition of nitrate of silver to a solution of an alkaline cyanide is to cause the reaction



Until the silver solution is added in excess of the quantity required for this reaction, the liquid remains perfectly clear, but a single additional drop causes a permanent turbidity of  $\text{AgCy}$ , or in presence of chlorides of  $\text{AgCl}$ . The process is extremely simple, the liquid to be tested being merely placed in a flask or beaker resting on a black surface, and decinormal nitrate of silver (17 grammes of  $\text{AgNO}_3$  per litre) being run in from a burette with continual agitation until a slight permanent turbidity results. Each c.c. of decinormal silver solution is equivalent to  $\cdot 0052$  of  $\text{Cy}$ ,  $\cdot 0054$  of  $\text{HCy}$ , or  $\cdot 00651$  of  $\text{KCy}$ . The above process only indicates the metallic cyanide present, free hydrocyanic acid giving an immediate precipitate with solution of silver. Hence, in assaying free hydrocyanic acid, the liquid must first be treated with a full equivalent of caustic alkali; but a very large excess should be avoided. The addition of the proper amount cannot be ascertained by litmus, cyanides of the alkali-metals having a powerfully alkaline reaction. The liquid at the termination of the titration should be distinctly alkaline to litmus; if otherwise, more caustic alkali must be added (which will cause the disappearance of the turbidity), and the titration continued till a permanent turbidity results. To compensate in accurate experiments for the slight error produced by a large excess of alkali, the liquid may be titrated back with normal acid, until a slightly increased turbidity results. For each 1 c.c. so used,  $\cdot 01$  c.c. should be deducted from the volume of decinormal  $\text{AgNO}_3$  previously employed. The correction is superfluous except in very accu-



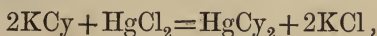
rate work. In a liquid containing alkaline cyanide as well as free hydrocyanic acid, the amounts of each of these may be ascertained by titrating first without addition of caustic alkali, and then continuing the process after adding it. The volume of silver solution first used represents the alkaline cyanide, the second quantity the free hydrocyanic acid.

In titrating medicinal hydrocyanic acid, 5 or 10 c.c. may be used; the liquid should be diluted with 12 to 20 volumes of water. Of Bitter-almond water 50 c.c. should be employed; it becomes milky on dilution. This may be avoided by adding alcohol, or the hydrocyanic acid may be determined gravimetrically, as described on page 32. Bitter-almond water and old solutions of cyanide of potassium are liable to give too high results by Liebig's process owing to the presence of ammonia, which has a solvent action on the cyanide of silver. Hence the end reaction does not occur so soon as it otherwise would. L. Siebold has shown that chloride when present may be conveniently determined in the same liquid in which the cyanide was estimated by nitrate of silver, by neutralising any excess of free alkali by cautious addition of dilute nitric acid, then adding chromate of potassium as an indicator, and continuing the addition of nitrate of silver till the red colour of the chromate of silver remains permanent. If cyanide only be present, the volume of silver solution now added will be exactly equal to that employed to obtain a permanent white turbidity; any excess over this amount represents the quantity of chloride present.\*

\* L. Siebold has pointed out that the double cyanides of silver with the alkali-metals are very permanent bodies, whilst their solutions are perfectly neutral to litmus. He has based on these facts, combined with Liebig's process, a very ingenious and accurate method of alkalimetry, which is directly applicable to the assay of alkaline carbonates. To the solution of a weighed quantity of the sample of carbonate, excess of hydrocyanic acid is added, and the liquid is at once titrated with standard nitrate of silver. As the production of permanent turbidity is only deferred in proportion to the amount of alkaline cyanide present (the excess of the hydrocyanic acid having no effect), and as carbonates are completely decomposed by hydrocyanic acid in presence of

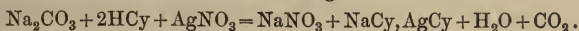
3. Another very convenient process for the volumetric determination of cyanides has been described by Mr J. B. Hannay.\*

It is based on the anomalous characters of cyanide of mercury, which substance is not decomposed by alkalies, and is at once produced on adding a mercuric solution to that of an alkaline cyanide. In practice, the process is conducted by adding a moderate excess of ammonia to the solution to be tested, placing the vessel on a black surface, and running in a decinormal solution of mercuric chloride (containing 13·55 grammes of  $\text{HgCl}_2$  per litre) with continual agitation until a permanent bluish-white opalescence is produced. As the reaction is expressed by the formula



each c.c. of mercurial solution (of the above strength) employed represents ·00651 gramme of  $\text{KCy}$ , or ·0026 of  $\text{Cy}$ , in the liquid examined. Very large proportions of ammonia interfere somewhat, but less than fifteen equivalents are without important effect. Alkaline sulphates, nitrates and chlorides do not interfere, nor do caustic or carbonated alkalies. Cyanates and thiocyanates are also without influence on the results, and the same is true of silver salts, so that the total cyanogen existing in electro-plating liquids can be directly determined by the process. The author's own experiments are

nitrate of silver, the volume of the latter solution added at once indicates the amount of alkali present, the reaction being



Hence, each c.c. of decinormal  $\text{AgNO}_3$  employed represents ·0062 of  $\text{Na}_2\text{O}$ , or ·0106 of  $\text{Na}_2\text{CO}_3$  in the sample taken. By boiling off the excess of free hydrocyanic acid and titrating again with nitrate of silver, using neutral chromate of potassium as an indicator, the proportion of chloride can be determined in the same quantity. Dr Siebold's test analyses are remarkably good, and he claims that the alkali and chlorine in a sample of soda-ash can both be determined in ten or fifteen minutes by the use of a single burette and standard solution. Strong hydrocyanic acid for use in the above process can readily be kept permanent by addition of glycerin (*Pharm. Journ.* 1878. Sept. 7, p. 191).

\* *Journ. Chem. Soc.* 1878, i. page 245.

not very favourable to the accuracy of Hannay's process, which, though useful, appears to give only approximate results.

4. Liebig's process may also be applied to the partial assay of electro-plating liquids, which commonly consist of a solution of the double cyanide of silver and potassium. There is frequently a considerable extra amount of cyanide of potassium present. This *only* will be indicated by titrating with nitrate of silver until a permanent turbidity results, 170 of  $\text{AgNO}_3$  representing 110.2 of free KCy. The cyanide of potassium existing in combination with cyanide of silver is best determined by Hannay's process (p. 35), or by estimating the silver itself (p. 38).

Any carbonate existing in alkaline cyanides or plating solutions may be determined by precipitating the liquid with calcium chloride, and collecting and weighing the resultant calcium carbonate.

5. FOR THE DETERMINATION OF CYANIDES, THIOCYANATES, FERROCYANIDES, AND FERRICYANIDES when the four classes of salts occur together in solution without heavy metals, the following method may be used:—A measured quantity of the liquid is strongly acidulated with hydrochloric acid, and precipitated with excess of ferric chloride. The precipitate of Prussian blue is filtered off, washed, boiled with caustic alkali, and the alkaline ferrocyanide produced filtered from the precipitated ferric hydrate and determined by titration with standard permanganate, or by one of the other methods described on page 47.

The filtrate from the ferric chloride precipitate is treated with ferrous sulphate and the liquid again filtered. The precipitate consists of ferrous ferricyanide, which on boiling with caustic alkali yields soluble ferrocyanide as described on page 50, test 5.

The filtrate from the precipitate produced by ferrous sulphate, which must contain excess of both ferrous and ferric salts, is treated with excess of soda and heated. It is then again



acidified with hydrochloric acid, when a precipitate of Prussian blue will result, the amount of which represents the simple cyanide originally present. It may be boiled with alkali, and the ferrocyanide produced titrated as before, and calculated to CN. The thiocyanate may be determined in the filtrate from the various iron precipitates by adding sulphite of sodium and cupric sulphate, or in a separate portion of the original liquid by oxidising it in acid solution with permanganate, and precipitating the resultant sulphate by barium chloride (see page 61, test 1).

6. For the method of determining the cyanogen in cyanide of mercury, see page 39.

7. A process of general applicability for the analysis of all solid cyanogen compounds without exception, is to ignite them at a full red heat with excess of soda-lime, when the whole of the cyanogen is converted into ammonia, which may be determined in the usual way and the cyanogen calculated from the amount found.

**Determination of the metals in Cyanides.**—The determination of metals existing in the form or in presence of simple and double cyanides, may be effected by the following methods:—

1. All cyanogen compounds, without exception, are completely decomposed, and the metals converted into sulphates or oxides, as the case may be, by treatment in platinum with a mixture of three parts of concentrated sulphuric acid and one part of water. On heating the mixture till nearly all the sulphuric acid is expelled, the residual mass will be obtained free from cyanogen. It may be dissolved in water or acid, and the metals determined by the usual methods. The process is not adapted for the analysis of cyanide of mercury, as some of the metal is volatilised. (When solid, cyanide of mercury may be ignited with soda-lime, and the volatilised mercury collected and weighed.)

2. From solutions containing the cyanides of mercury, silver,



or cadmium, the heavy metal may be precipitated by passing sulphuretted hydrogen, and the same process is applicable to solutions of zinc, if sulphide of sodium or potassium be substituted for the sulphuretted hydrogen. The following method has been largely employed by the author for the determination of the metallic silver in electro-plating liquors.

A definite measure of the sample liquid is largely diluted with water, and the whole raised to boiling. Sulphuretted hydrogen is passed through the liquid, or sulphide of ammonium gradually added. The silver falls as a black sulphide, which is liable to be contaminated with copper and zinc. The washed precipitate is rinsed off the filter into a flask or beaker and treated with excess of bromine-water, which converts it rapidly and completely into argentic bromide. If any sulphur appears to have separated, a drop of bromine should be added to the residue so as to ensure complete oxidation. Boiling water is now added, and the bromide of silver is washed, dried, fused and weighed. 188 parts by weight of the precipitate represent 108 of metallic silver.

3. For the determination of the precious metal contained in the solution of the double cyanide of gold and potassium used for electro-gilding, the author has found the following method very satisfactory.

A measured quantity of the gilding solution is introduced into a porcelain crucible and cautiously concentrated; when in a syrupy condition, a few grammes of pure red-lead or litharge are added, and the evaporation is continued to complete dryness. There is little or no tendency to spitting. The crucible containing the residue is covered and raised for a short time to a moderate red heat. The oxide of lead is reduced by the cyanide present, with production of metallic lead and cyanate, and the reduced metal unites with the gold. The resultant button of metal is separated from the slag, and the gold obtained from the alloy either by cupellation or treatment with pure nitric acid.

Electro-silvering solutions may be assayed in a

precisely similar manner, but in this case treatment of the rich lead with nitric acid is inadmissible and cupellation *must* be resorted to.

The amount of precious metal found in an electro-depositing liquid is commonly reported in troy ounces, pennyweights, and grains per pint of solution.

**Mercuric Cyanide.**  $\text{HgCy}_2$ .—This is almost the only simple cyanide of a heavy metal which is soluble in water. Owing to its stability it reacts in an anomalous manner. Thus, it does not respond to the iron test for cyanides (No. 3, page 29), and is not precipitated by nitrate of silver. It yields, however, a yellowish white precipitate of palladious cyanide on addition of palladious nitrate. Cyanide of mercury is not precipitated by alkalies. By boiling with hydrochloric acid, hydrocyanic acid is evolved, and mercuric chloride formed. Solution of mercuric cyanide is readily decomposed by sulphuretted hydrogen, and, after separation from the precipitated mercuric sulphide, the cyanide in the liquid can readily be detected by Liebig's test (No. 4, page 29). Cyanide of mercury may also be decomposed by digesting the solution with metallic cadmium, which precipitates metallic mercury and forms cadmium cyanide,  $\text{CdCy}_2$ , in which the cyanogen is readily determined.

Owing to the tendency to form mercuric cyanide, many simple and compound cyanides are decomposed by boiling with yellow mercuric oxide and water. This is true of ferro- and ferri-cyanides of potassium and of Prussian blue, but not of cobalticyanides. No mercurous cyanide is known; on adding mercurous nitrate to a liquid containing hydrocyanic acid, or a metallic cyanide, metallic mercury separates, and soluble mercuric cyanide is formed. A similar reaction occurs on treating calomel with excess of hydrocyanic acid.

When dry mercuric cyanide is heated it gives metallic mercury, paracyanogen, and cyanogen gas. A hot solution of mercuric cyanide readily dissolves yellow mercuric oxide.

**Potassium Cyanide.**  $\text{KCN} = \text{KCy}$ .—This salt is an important commercial product, the assay of which is frequently required. It always results from the ignition of nitrogenous organic matter with caustic or carbonated alkali, but is usually prepared by heating a mixture of carbonate and ferrocyanide of potassium to dull redness, when the following reaction occurs:—

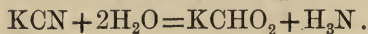


As prepared by this process the product always contains cyanate, and usually carbonate; sulphide is also present if the alkali used contained any sulphate. By heating the ferrocyanide alone, or by adding charcoal or sodium to the mixture, the formation of cyanate may be avoided.

Cyanide of potassium fuses at a low red heat to a transparent liquid, which is a most powerful reducing agent, liberating tin, antimony, bismuth, lead, &c., from their oxides and sulphides, with formation of potassium cyanate or thiocyanate. The thiocyanate also results from fusing the cyanide with free sulphur or a thiosulphate (hyposulphite), or by boiling the aqueous solution with sulphur.

Cyanide of potassium seems to volatilise unaltered at a white heat. It is frequently produced on a considerable scale in blast-furnaces. When heated in the air it forms cyanate, and in presence of vapour of water potassium carbonate and ammonia result.

Cyanide of potassium generally occurs in cakes or rods, but it may be obtained in cubes by crystallisation from hot alcohol. It is very deliquescent and soluble in water, forming an alkaline and intensely poisonous liquid. It may be kept unaltered in close vessels, but in the air it absorbs carbonic acid with liberation of hydrocyanic acid. By passing a stream of carbonic acid gas through the aqueous solution the cyanide may be completely decomposed. On boiling the aqueous solution, formate of potassium and ammonia are produced:—



Cyanide of potassium unites with most of the cyanides of the heavy metals forming more or less stable double cyanides much used in electro-metallurgy. The methods of assaying and analysing these bodies have been already described (pages 36 and 38). Owing to the strong tendency which exists to form a double cyanide of potassium and silver, cyanide of potassium dissolves all silver salts except the sulphide. Hence its employment as a fixing agent in photography.

The proportion of real cyanide present in commercial cyanide of potassium may be ascertained with facility by Liebig's or Hannay's volumetric method (see pages 33 and 35). The latter process is preferable in presence of ammonia, which is often met with in wet cyanide or old solutions.

Cyanide of potassium to be used for electro-gilding should contain 90 per cent. of real KCy. For electro-plating liquids 70 per cent. is pure enough, while for photographic purposes 40 or 50 per cent. samples are sufficiently pure.

The various impurities commonly met with in potassium cyanide may be looked for in the following manner:—

CARBONATE OF POTASSIUM will remain insoluble on treating the powdered sample with hot alcohol of '849 sp. gr.

CYANATE OF POTASSIUM will dissolve in alcohol of the above strength, and the solution will evolve carbonic acid on treatment with hydrochloric acid; or, on adding water and boiling off the alcohol, the liquid will give a precipitate of calcium carbonate on adding calcium chloride. (See also page 54.)

CHLORIDE OF POTASSIUM can be detected by reaction 2 b. page 28, and be determined as described on page 32, or by Siebold's volumetric method (page 34).

FORMATE causes the salt to blacken on ignition. It is more certainly detected by precipitating the cold dilute solution of



the sample by excess of nitrate of silver, filtering cold, and heating the clear liquid. In presence of a formate metallic silver is precipitated. The filtrate from the precipitate produced by silver nitrate will also give a red colour with ferric nitrate or sulphate if a formate be present.

FERROCYANIDE will give a Prussian blue precipitate on adding ferric chloride (free from any trace of ferrous chloride) to the solution after acidulating it with hydrochloric acid.

THIOCYANATE (sulphocyanide) of potassium will give a deep red colour on application of the last test.

SILICATE can be detected and estimated in the ordinary way by evaporation to dryness with hydrochloric acid, the residue insoluble in acidulated water being silica.

SULPHATE is detected by addition of barium chloride to the acidulated solution of the sample.

SULPHIDE will give a black precipitate with mercuric chloride, and yellow with a solution of cadmium. It is best separated by agitating the solution of the sample with freshly-precipitated lead carbonate.

FREE AMMONIA can be recognised by the smell.

### **FERROCYANIDES.** $4\text{MCy}$ , $\text{FeCy}_2 = \text{M}_4\text{FeCy}_6 = \text{M}_4\text{Cfy}$ .

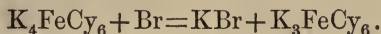
These salts may be regarded as compounds of ferrous cyanide with the cyanide of some other metal or basylous radical. Neither the iron nor the cyanogen is recognisable by the ordinary tests, and the ferrocyanides as a class are not poisonous. Many of them have highly characteristic properties. Ferrocyanides of the light metals are soluble, but most of those of the heavy metals are insoluble.

An aqueous solution of potassium ferrocyanide gives the following reactions :—

1. On adding strong hydrochloric acid to a concentrated solution of potassium ferrocyanide, hydroferrocyanic acid is set free, and, on adding ether and shaking, is precipitated in white crystalline scales. These are readily soluble in

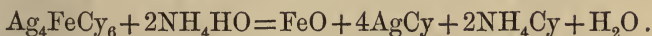
water and alcohol. The solution is strongly acid, and absorbs oxygen from the air, with formation of Prussian blue.

2. Chlorine, bromine, hydrogen dioxide, permanganate or chromate in acid solution, and other oxidising agents convert the ferrocyanide into ferricyanide; thus—



3. When boiled with yellow mercuric oxide, oxide of iron is precipitated, while mercuric cyanide and caustic and carbonated alkali remain in solution. All ferrocyanides react similarly.

4. Nitrate of silver precipitates white argentic ferrocyanide,  $\text{Ag}_4\text{Cfy}$ , insoluble in dilute nitric acid. The precipitate is insoluble in cold ammonia, but on boiling is decomposed thus—



5. Cupric sulphate added in excess precipitates chocolate-red cupric ferrocyanide,  $\text{Cu}_2''\text{Cfy}$ . In insufficient quantity, brown  $\text{K}_2\text{Cu}''\text{Cfy}$  is formed. The precipitates are insoluble in acetic or hydrochloric acid, but soluble in ammonia.

6. Zinc sulphate precipitates white ferrocyanide of zinc,  $\text{Zn}_2''\text{Cfy}$ , insoluble in hydrochloric acid. When a strongly ammoniacal solution of zinc is heated to boiling, and ferrocyanide added, a white precipitate is obtained. This reaction is a very delicate test for zinc.

7. Ferrous sulphate (when quite free from ferric salt) precipitates white potassio-ferrous ferrocyanide,  $\text{K}_2\text{Fe}''\text{Cfy}$ , which rapidly turns blue in the air.

8. Ferric chloride precipitates Prussian blue, ferric ferrocyanide,  $\text{Fe}_4''' \text{Cfy}^{\text{iv}}_3 = \text{Fe}_5\text{Cy}_{18} = 3\text{FeCy}_2, 2\text{Fe}_2\text{Cy}_6$ . With an insufficient quantity of ferric salt, a compound is produced which is insoluble in saline solutions, but dissolves in pure water, forming "soluble Prussian blue." Ferric ferrocyanide is insoluble in dilute mineral acids, but dissolves in oxalic

acid to a deep blue liquid (sometimes used as an ink), and in ammonium tartrate to a violet liquid.

When boiled with caustic alkalis or magnesia, ferric ferrocyanide (Prussian blue) is decomposed with precipitation of ferric hydrate and formation of a soluble ferrocyanide.

The formation of Prussian blue furnishes the most delicate and characteristic test for ferrocyanides. It is also applied to the detection of simple cyanides and hydrocyanic acid. (See page 29.)

THE DETERMINATION OF FERROCYANIDES in solution may be effected by the following volumetric method. Thiocyanates, sulphites, sulphides, thiosulphates and other reducing agents must be absent. The process is well adapted for the assay of ferrocyanide of potassium in the absence of these impurities.

A quantity of material, containing about .2 gramme of potassium ferrocyanide, is dissolved in, or diluted with water to about 200 c.c., and the liquid is placed in a white basin. The solution is acidified with sulphuric acid, and standard solution of permanganate of potassium is run in till the yellow colour of the liquid changes to yellowish red. The end reaction is tolerably definite. If a trace of ferric chloride be added to the liquid, the disappearance of the bluish green colour will render the termination still more distinct. The reaction is :  $5K_4FeCy_6 + KMnO_4 + 4H_2SO_4 = 5K_3FeCy_6 + 3K_2SO_4 + MnSO_4 + 4H_2O$ .

The permanganate is preferably set by titrating a known quantity of pure potassium ferrocyanide,\* but the ordinary decinormal solution may be employed. Each c.c. of decinormal permanganate used represents 0.04224 of crystallised, or 0.03684 of anhydrous potassium ferrocyanide.

From salts of all other kinds than chlorides, bromides, iodides, iodates, cyanides, thiocyanates, ferricyanides, and sul-

\* It must not be forgotten that the crystallised salt contains three atoms of water ( $K_4Cfy + 3H_2O$ ).

phides, ferrocyanides may be separated by precipitating the liquid with nitrate of silver in presence of free nitric acid.

From chlorides and bromides (and thiocyanates) ferrocyanides may be separated by sulphate of copper in presence of free acid, and from these salts and ferricyanides by precipitation with ferric sulphate.

In the filtrate from the copper precipitate, after removing the excess of copper by sulphuretted hydrogen, the alkaline base of soluble ferrocyanides can be conveniently determined.

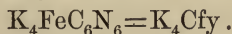
Prussian blue and other insoluble ferrocyanides (the silver salt imperfectly) are converted into ferrocyanide of potassium by boiling with solution of caustic potash, the heavy metal being usually precipitated as oxide. If soluble in potash solution, it may be got rid of by passing carbonic acid gas through the liquid, or in some cases magnesia may be substituted for the potash. In the filtrate, the ferrocyanide can be determined by standard permanganate or other means.

Other methods for the determination of ferrocyanides are given under the head of "Potassium Ferrocyanide" on page 47, *et seq.* General information will also be found under "Metallic Cyanides," pages 36 and 37.

**Potassium Ferrocyanide.**—Yellow prussiate of potash. Ferro-prussiate of potash.

*French*—Prussiate jaune de potasse.

*German*—Ferrocyankalium, or Blutlaugensalz.



This important salt crystallises in amber yellow, deeply truncated octohedra of the quadratic system,\* often having the appearance of tables. The crystals have a very perfect cleavage at right angles to the principal axis. In a crystalline state it contains  $3\text{H}_2\text{O}$ , the whole of which is expelled at  $100^\circ\text{C}$ . At a red heat the salt is decomposed into cyanide of potassium, carbide of iron, and nitrogen gas.

\* The crystalline form of potassium ferrocyanide is, according to recent researches, more probably monoclinic.



Ferrocyanide of potassium is tolerably stable at ordinary temperatures, both in the solid state and in solution. It has a perfectly neutral reaction, and is not poisonous.

Dilute acids liberate hydroferrocyanic acid; by moderately dilute hot sulphuric acid the salt is decomposed with evolution of hydrocyanic acid (see page 22). When heated with excess of strong sulphuric acid, carbon monoxide is evolved as gas, and sulphates of potassium, ammonium and iron are formed:

$$\text{K}_4\text{FeC}_6\text{N}_6 + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} = 6\text{CO} + 2\text{K}_2\text{SO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + \text{FeSO}_4.$$

Ferrocyanide of potassium is soluble in four parts of cold or two of boiling water. It is insoluble in alcohol.

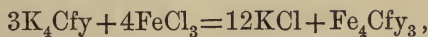
The reactions of a solution of potassium ferrocyanide are given on pages 42 and 43.

Ferrocyanide of potassium is manufactured by heating carbonate of potassium with horns, hoofs, dried blood, wool and hair clippings, feathers, leather parings, or other animal refuse. Scrap-iron is sometimes added, but in other cases the manufacturer relies on the iron of the vessel employed, which is made of great thickness on purpose. The mass obtained is lixiviated with water, and the ferrocyanide separated and purified by crystallisation. If the carbonate of potassium contain more than about 3 per cent. of sodium carbonate, the crystallisation is interfered with. The first crop of crystals (or "prussiate scale") contains about 97 per cent. of hydrated ferrocyanide, and on recrystallisation it is obtained with 99.8 per cent. The usual impurities are sulphate, sulphite, sulphide, thiosulphate (hyposulphite), chloride and carbonate of potassium. Very considerable quantities of sulphate are sometimes present, which may be detected and estimated by barium chloride. In addition to these impurities, the mother-liquors contain sodium salts, thiocyanate (sulphocyanide), silicate, &c.

1. The mother-liquors from ferrocyanide works may be assayed for ferrocyanide as follows:—Remove any sulphide by boiling the liquid with carbonate of lead; filter, acidify the filtrate with dilute sulphuric acid, and add from a burette a standard

solution of cupric sulphate, containing 10 grammes of the crystallised salt to the litre. The addition is continued until a strip of filter-paper, immersed so that the clear liquid may rise by capillary attraction, gives no blue colour when touched with a drop of ferric chloride. The precipitating power of the copper solution is ascertained by means of pure potassium ferrocyanide. About .2 gramme of the salt should be used, dissolved in 50 c.c. of water. Thiocyanates (sulphocyanides) do not interfere with this method.

2. Instead of using cupric sulphate, a solution of ferric sulphate or chloride may be employed. When this is added with vigorous agitation to a liquid containing ferrocyanide of potassium a deep blue liquid results, which on a further addition becomes turbid, and when exactly sufficient iron solution has been added for the reaction,



the Prussian blue coagulates, and the liquid becomes perfectly clear. The end reaction may also be observed as in the last process. If thiocyanates be present, the least excess of iron solution will cause the liquid to assume a deep red colour. The change from blue to red furnishes a very definite end-reaction.

This process may be conveniently employed for the assay of ferrocyanide in dye-vats and in "metal," which is the name given to the crude product in the manufacture of ferrocyanide. In the case of alkaline liquids, the solution must be first acidulated with dilute sulphuric or nitric acid.

3. Another volumetric method of estimating ferrocyanide, but which is not applicable in presence of thiocyanates or other reducing agents, is described on page 44.

4. A very simple method of determining small quantities of ferrocyanides present in soda-lyes has been recently described by Dr Hurter of Widnes.\* These

\* *Chemical News*, xxxix. p. 25.

liquors contain sodium ferrocyanide, cyanate, and thiocyanate, but of these the first only is objectionable, on account of the brownish colour it imparts to the finished product. Cyanide of sodium may occasionally be present, in which case it may be converted into ferrocyanide by a small quantity of ferrous sulphate, boiling and filtering. The following are the details of Dr Hurter's method:—100 c.c. of the strong soda-lye are boiled with solution of bleaching powder in quantity sufficient to convert all sulphides and thiosulphates into sulphates, and the ferrocyanide into ferricyanide. The liquid is then acidified and freed, as far as possible, from the excess of chlorine by warming and agitating it. It is then titrated with a  $\frac{1}{20}$ th normal solution of cupric nitrate, prepared by dissolving 3.170 grammes of metallic copper in as little nitric acid as possible, and diluting to 1 litre. On adding this solution to the acidulated liquid containing ferricyanide, a yellow precipitate of cupric ferricyanide is formed. Drops of the thoroughly-mixed liquid are taken up with a glass rod, and added to drops of a 1 per cent. solution of crystallised ferrous sulphate on a porcelain plate. As long as insufficient copper solution has been added to combine with the whole of the ferricyanide present, the deep blue ferrous ferricyanide is formed on the porcelain. When the liquid no longer contains soluble ferricyanide, the indicator acts on the copper precipitate, and reduces it to the characteristic chocolate-coloured cupric ferrocyanide. Hence, the end of the reaction is indicated by a brown colour being produced on the porcelain instead of the blue first obtained. Each c.c. of the copper solution added before this result is obtained represents .01013 gramme of sodium ferrocyanide in the liquid. The method is not suitable for the determination of large quantities of ferrocyanides, as the colour of the copper precipitate obscures the blue colour, and the precipitate is not always of definite composition.

It is evident that this process is adapted for the direct esti-

mation of small quantities of ferricyanide, into which the ferrocyanide has first to be converted.

**Ferric Ferrocyanide, or Prussian Blue,**  $\text{Fe}_4\text{Cfy}_3$ , is obtained in the manner, and has the properties described on page 43. It is prepared on a large scale for use as a blue colouring-matter. When dry it forms a dark blue mass, having a strong coppery lustre and conchoidal fracture. Commercial Prussian blue often contains a considerable admixture of potassio-ferrous ferricyanide,  $\text{KFe}''\text{Cfdy}$ .

Prussian blue is often adulterated with alumina, starch, calcium carbonate, &c. The last may be detected by the powder effervescing on addition of dilute hydrochloric acid. In the solution obtained by digestion with the acid for some time, alumina may be detected by addition of ammonia. Starch may be detected by boiling the sample with water, which will produce paste in presence of much starch. Smaller quantities may be detected by digesting the finely-powdered sample with magnesia and water in the cold; the residue is filtered and washed, and treated with cold dilute hydrochloric acid. The oxide of iron and excess of magnesia are dissolved, and the residual starch can be weighed, examined under the microscope, and tested with iodine. Any China clay and sulphate of barium will remain with the starch, and, after removing the latter by ignition or boiling with water, the residue may be examined with a view to their recognition.

The colouring power of Prussian blue may be tested by grinding the sample with a large proportion of white-lead and oil, and comparing the colour with that given by a standard sample of known purity.

The characteristics of good Prussian blue are lightness; a deep, fine, blue colour, with a coppery lustre; and the sample should adhere strongly to the tongue. It should not effervesce with acids, nor thicken when boiled in water.

The proportion of real ferrocyanide contained in Prussian blue may be determined by treating the sample with caustic



alkali, filtering from the oxide of iron, and determining the ferrocyanide in the filtrate, as described on page 44, *et seq.*

**FERRICYANIDES.**  $3\text{MCy}, \text{FeCy}_3 = \text{M}_3\text{FeC}_6\text{N}_6 = \text{M}_3\text{Cfdy}.$

These salts may be regarded as compounds of ferric cyanide with the cyanide of some other metal or basylous radical. Neither the iron nor the cyanogen can be recognised by the ordinary tests, and the ferricyanides as a class are not violently poisonous. The ferricyanides of the light metals have a red colour, and are soluble in water. The ferricyanides of the heavy metals are mostly insoluble.

An aqueous solution of potassium ferricyanide gives the following reactions:—

1. Sulphuretted hydrogen is readily oxidised with formation of a ferrocyanide.

2. In presence of caustic alkali, stannous, manganous, ferrous, plumbous, and chromic oxides are further oxygenated with formation of ferrocyanide. Alcohol, oxalates, cyanides, sulphites, and phosphites are also oxidised, and indigo is bleached. Sugar, starch, and cellulose also reduce ferricyanide.

3. When boiled with yellow oxide of mercury and water, ferricyanides are completely decomposed with formation of mercuric cyanide and precipitation of oxide of iron.

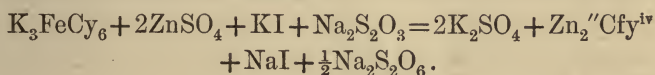
4. Nitrate of silver precipitates orange-red argentic ferricyanide,  $\text{Ag}_3\text{FeCy}_6$ , insoluble in dilute nitric acid, but soluble in ammonia.

5. Ferrous sulphate produces a deep blue precipitate (Turnbull's blue) of ferrous ferricyanide,  $\text{Fe}_3''(\text{FeCy}_6)_2$ , insoluble in dilute acids, but decomposed by hot caustic alkali with formation of soluble ferrocyanide and black ferroso-ferric oxide. This reaction distinguishes it from Prussian blue, which in appearance it closely resembles, but which yields yellow-brown ferric oxide (hydrated) without any ferrous oxide, on boiling with alkalies.

6. Ferric chloride (if free from ferrous salt) produces merely a brownish coloration in solution of ferricyanides free from ferrocyanides. This liquid is a very delicate test for deoxidising bodies which cause the formation of a blue precipitate.

1. FERRICYANIDES MAY BE DETERMINED by boiling with ferrous sulphate and caustic alkali, filtering and determining the ferrocyanide in the filtrate by permanganate (see page 44). Sulphite or thiosulphate of sodium may be substituted for the ferrous sulphate, if the process with a ferric solution described on page 47 be substituted for the permanganate. In either case, any ferrocyanide existing in the sample is determined in a separate portion, and the quantity subtracted from the total amount found.

2. Another method is to mix the dilute solution of the ferricyanide with iodide of potassium and hydrochloric acid in excess, add an excess of solution of iron-free sulphate of zinc, neutralise the free acid with a slight excess of bicarbonate of sodium, and determine the liberated iodine by standard thiosulphate (hyposulphite) of sodium and starch. The reaction is,



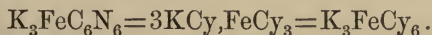
Each c.c. of decinormal thiosulphate required to react on the liberated iodine represents 0.0329 grammes of potassium ferricyanide.

3. A very simple and fairly accurate method of determining small quantities of ferricyanides is described on page 48.

**Ferricyanide of Potassium.**—Potassium ferridecyanide. Red prussiate of potash.

*French*—Prussiate rouge de potasse.

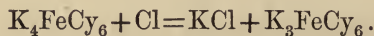
*German*—Ferridcyanalium, or Rothesblutlaugensalz.



This salt crystallises in ruby-red monoclinic prisms, which are anhydrous. The salt has an aperient action, but is not poison-

ous. It is soluble in  $2\frac{1}{2}$  parts of cold, or  $1\frac{1}{4}$  of boiling water. The solution has a strong yellow colour. By exposure to light, or evaporation to dryness, it is partially decomposed with formation of ferrocyanide.

The salt is manufactured in practice by acting on coarsely-powdered potassium ferrocyanide by chlorine gas, the reaction being—



The product is dissolved in water, and separated from the potassium chloride by crystallisation. The mother-liquor is employed for preparing Turnbull's blue (page 50) by precipitation with ferrous sulphate. The crude mixture of potassium ferricyanide and chloride is sometimes employed direct by calico printers.

By the action of heat and strong acids, potassium ferricyanide is decomposed in a very similar manner to the ferrocyanide (pages 45 and 46). By the action of iodine on its hot solution, potassium ferricyanide is converted into a new salt of the formula  $\text{K}_2\text{FeCy}_6$ .

The qualitative reactions of a solution of potassium ferricyanide are described on page 50, and the methods for its quantitative determination on page 51.

**Nitro-ferricyanides ; Nitroprussides.**—The only one of these salts of special interest is the potassium compound,  $\text{K}_2\text{FeCy}_5\text{NO}$ , which results from the action of nitric or nitrous acid on ferro- or ferri-cyanide of potassium. With soluble sulphides, potassium nitroprusside gives a beautiful but transient violet colour, and with ferrous or zinc salts a salmon-coloured precipitate. The last reaction distinguishes nitroprussides from cyanides of the formula  $\text{M}_2\text{FeCy}_6$ , which give a green precipitate with zinc sulphate.

**COBALTICYANIDES.**  $3\text{MCy}, \text{CoCy}_3 = \text{M}_3\text{CoCy}_6.$

This very permanent class of double cyanides is chiefly of interest from its application to the separation of nickel and

cobalt. When cyanide of potassium is added to a solution of cobalt, brownish-white cobaltous cyanide,  $\text{CoCy}_2$ , is formed; this dissolves in excess of potassium cyanide to form the easily decomposable double cyanide  $2\text{KCy}, \text{CoCy}_2$ . With excess of potassium cyanide, red cobalto-cyanide of potassium is formed,  $\text{K}_4\text{CoCy}_6$ . On heating the solution containing this, it is quickly converted into colourless very stable cobalticyanide of potassium,  $\text{K}_3\text{CoCy}_6$ , analogous to the ferricyanide. The change occurs with evolution of hydrogen. A more perfect reaction occurs on treating the cold solution with chlorine or bromine. The resultant solution of cobalticyanide of potassium is not decomposed by boiling with mercuric oxide. This reaction enables nickel to be separated from cobalt, the former of which is wholly precipitated, and remains as  $\text{NiO}$  on igniting the precipitate. The same reaction distinguishes cobalticyanides from ferro- and ferri-cyanides. Cobalticyanides give no precipitate with ferric salts. They are completely precipitated from acid solutions by sulphate of nickel, the precipitate leaving  $\text{Ni}_3 + \text{Co}_2$  by ignition in the air and subsequent reduction in hydrogen. Mercurous nitrate completely precipitates cobalticyanides from neutral solutions, the precipitate leaving  $\text{Co}_3\text{O}_4$  on ignition. Cobalticyanides are completely decomposed by heating with concentrated sulphuric acid (page 37).

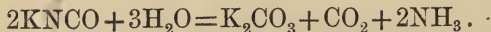
## CYANATES.

**Oxycyanides.**  $\text{MCNO} = \left. \begin{matrix} \text{CN} \\ \text{M} \end{matrix} \right\} \text{O} = \left. \begin{matrix} \text{CO}'' \\ \text{M} \end{matrix} \right\} \text{N}^* \text{—These salts are of but little importance except in a few cases. Their general reactions and properties may be inferred from those of}$

\* From the recent researches of Bannow and others, the ordinary cyanates probably correspond to the last of these formulæ, and hence are strictly isocyanates. In confirmation of this view, a cyanate of potassium, which is probably the normal salt, has been obtained by the action of caustic potash on cyanogen chloride. This salt differs from ordinary (iso-) cyanate of potassium by crystallising from its alcoholic solution in long thin needles instead of in scales resembling the chlorate.



**Cyanate of Potassium, KNCN.**—This salt is obtained by fusing potassium cyanide or ferrocyanide with litharge or manganese dioxide. The salt is not decomposed by mere ignition, but, in presence of moisture or by evaporation of its aqueous solution, it splits up as follows :—

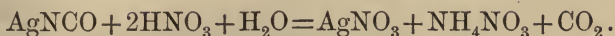


This reaction is the cause of the ammoniacal smell of deliquesced commercial cyanide of potassium, which often contains much cyanate. On addition of moderately concentrated sulphuric or hydrochloric acid to potassium cyanate, cyanic acid is evolved, having a pungent odour resembling acetic acid, and most powerfully affecting the eyes. The odour is slowly but very well developed by treating a solution of the cyanate with acid tartrate of potassium.

CYANIC ACID is extremely unstable, becoming rapidly converted in cyanamide ( $\text{C}_2\text{N}_2\text{H}_2\text{O}_2$ ). The greater part of the acid is decomposed in the act of liberation with formation of carbonic anhydride and ammonia, which latter remains in combination with the mineral acid used. ( $\text{HNCO} + \text{H}_2\text{O} = \text{H}_3\text{N} + \text{CO}_2$ ). Hence cyanates, on addition of an acid, effervesce and evolve much carbonic acid smelling of cyanic acid, and the resultant liquid gives off ammonia when boiled with slaked lime or caustic alkali. It is evident that these reactions are insufficient for the recognition of a cyanate when, as in commercial cyanide of potassium, a carbonate and cyanide are also present. The detection of cyanate in commercial cyanide of potassium is described on page 41.

The determination of cyanate, when existing in the form of pure cyanate of potassium, may be effected by the following process devised by the author :—One gramme of the sample is dissolved in very cold water, and precipitated without delay by the addition of excess of a neutral solution of nitrate of silver. The precipitate of argentic cyanate is filtered off and washed slightly. It is then dissolved in a moderate excess of

warm normal nitric acid, when the following reaction takes place:—



Hence, one atom of cyanate will neutralise two of nitric acid. The liquid is filtered from any trace of insoluble matter and titrated with normal alkali. Each c.c. of normal nitric acid neutralised by the cyanate represents  $\cdot 1622$  of  $\text{KNCO}$  in the sample taken. The author obtained 101·6 and 101·2 per cent. in two experiments made by this process on pure potassium cyanate. Probably the same process might be applied to the determination of cyanate in commercial cyanide of potassium, the carbonate being first separated by precipitating the cold solution with barium or calcium nitrate. As the cyanide and any chloride which may be present will be precipitated as silver salts together with the cyanate, the subsequent treatment with warm dilute nitric acid will leave an insoluble residue, which must be separated before titrating with alkali.

**Cyanate of Ammonium** ( $\text{NH}_4, \text{NCO}$ ) may be obtained by decomposing cyanate of silver by solution of ammonium chloride, or cyanate of potassium or barium by ammonium sulphate. It is extremely unstable, the solution being converted by evaporation into urea,  $\left. \begin{array}{c} \text{CO} \\ \text{H}_4 \end{array} \right\} \text{N}_2$  or  $\left. \begin{array}{c} \text{NH}_3(\text{CN}) \\ \text{H} \end{array} \right\} \text{O}.$

## THIOCYANATES.

**Sulphocyanates; Sulphocyanides.**  $\text{MCNS} = \begin{array}{c} \text{CN} \\ \text{M} \end{array} \left. \right\} \text{S}.$

—These salts are the sulphur analogues of the cyanates, but are of a more stable character than the latter salts. Decided traces of thiocyanates exist in the saliva, and they may also be detected in the urine; hence they appear to pass through the system unaltered. In the saliva the presence of thiocyanates is directly indicated on addition of ferric chloride. For their detection in urine the liquid is precipitated by baryta water, the filtrate evaporated to a syrup, extracted with alcohol,

the solution so obtained again evaporated, the residue redissolved in water, decolorised by charcoal, and tested by ferric chloride, &c.

Thiocyanates are present also in the ammoniacal liquor and gas-lime obtained in the purification of coal-gas, and are produced in several important reactions.

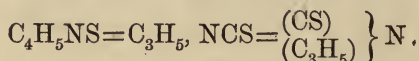
ISO-THIOCYANATE OF ALLYL (see below) constitutes the natural essential oil of mustard.

As a class, the thiocyanates are very poisonous, and have as deleterious effect on plants as on animals.

The general characters of the thiocyanates, with methods for their detection and estimation, are given in detail under the head of potassium thiocyanate.

**Allyl Iso-Thiocyanate.**—Sulphocyanide of allyl; allyl thiocarbimide (*Volatile Oil of Mustard*).

*French*—Essence de moutarde. *German*.—Senföl



This substance was formerly mistaken for the normal thiocyanate. It may be produced artificially by several reactions. It also results from the treatment of black mustard (*Sinapis nigra*) and other cruciferous seeds with water, with subsequent distillation. Its production depends on the presence of a body called myrosin existing to a small extent in the black, and to the extent of about 15 per cent. in white mustard-seed. Myrosin is soluble in water, but is coagulated and rendered inactive by heat or alcohol. The black mustard also contains the potassium salt of myronic acid ( $\text{H},\text{C}_{10}\text{H}_{18}\text{NS}_2\text{O}_{10}$ ), and, under the influence of the ferment myrosin in presence of water, this splits up into oil of mustard, glucose, and acid sulphate of potassium.



As myronic acid is not present in white mustard, no volatile oil of mustard can be obtained from that alone. The myrosin

in black mustard being limited in quantity, the best yield of oil is obtainable from a mixture of white and black mustards. When the reaction with cold water has taken place the mixture is distilled. The acrid taste of white mustard is due to the presence of sinalbin ( $C_{30}H_{44}N_2S_2O_{16}$ ), which under the influence of myrosin and water is said to give rise to acrinyl thiocyanate, sulphate of sinapine ( $C_{16}H_{23}NO_5 \cdot H_2SO_4$ ), and glucose. The first of these is the acrid volatile oil. It is produced in very small quantity.

Black mustard yields about  $\frac{1}{2}$  per cent. of its weight of volatile oil on treatment with water followed by distillation.

Iso-thiocyanate of allyl is an oily liquid of a light yellow colour. It has a density of 1.015, and boils at about  $147^\circ C$ . It smells powerfully of mustard, and the vapour excites tears. It has a burning, mustard-like taste, and rapidly blisters the skin. It mixes with strong sulphuric acid without great coloration, but decomposition subsequently ensues. Heated in alcoholic solution with zinc and hydrochloric acid, it evolves sulphuretted hydrogen and marsh-gas, and forms allyl-amine ( $C_3H_5 \cdot H_2N$ ). Boiled with caustic soda and a little acetate of lead, oil of mustard yields black sulphide of lead. When heated with strong nitric acid or bromine, oil of mustard yields a number of products, among which sulphuric acid may be recognised by diluting largely and adding barium chloride.

Oil of mustard is occasionally prepared artificially by distilling sulphate or iodide of allyl ( $C_3H_5I$ ) with potassium thiocyanate. A sample, probably prepared in the former manner, was found by Dr E. Mylius to contain: Allyl-iso-thiocyanate, 92.2 per cent.; carbon disulphide, 0.8 per cent.; hydrocyanic acid, .02 per cent.; polysulphides (chiefly allyl-trisulphide), 4.0 per cent.; and, non-volatile bodies containing both nitrogen and sulphur, 3.0 per cent. According to C. Schacht, this must have been an exceptionally impure sample.



The purity of oil of mustard may be tested in the following manner:—If two or three drops of the sample be allowed to fall on water, they should sink to the bottom on very slight agitation and should remain perfectly clear. A slight admixture with petroleum spirit causes the drops to remain at the surface. If the oil contains 5 per cent. of strong alcohol the drops will become opalescent. Five drops of pure oil of mustard dissolve in fifty of strong sulphuric acid to a clear deep yellow liquid. Other vegetable oils become charred, and carbon disulphide separates in minute drops which render the liquid turbid.

**Ammonium Thiocyanate.**  $\text{NH}_4\text{CNS} = \left. \begin{array}{c} \text{CN} \\ \text{NH}_4 \end{array} \right\} \text{S}$ .—This salt results from the distillation of coal, and is found in considerable quantities in the ammoniacal liquor of the gas-works. Commercial sulphate of ammonium often contains thiocyanate. Ammonium thiocyanate is produced by various reactions (see method 4 for detecting hydrocyanic acid, page 29), including the action of carbon disulphide on ammonium sulphide  $(\text{NH}_4)_2\text{S} + \text{CS}_2 = \text{NH}_4\text{CNS} + 2\text{H}_2\text{S}$ . Commercial thiocyanate of ammonium forms colourless deliquescent crystals which are very soluble in water and alcohol, the solution taking place with great reduction of temperature. The dilute aqueous solution is perfectly permanent. The reactions of ammonium thiocyanate are strictly analogous with those of the potassium salt (see page 59).

When kept at a temperature of  $170^\circ \text{C}$ . for some time, ammonium thiocyanate becomes converted into sulphurea,  $\left. \begin{array}{c} \text{CS} \\ \text{H}_4 \end{array} \right\} \text{N}_2 = \left. \begin{array}{c} \text{NH}_3(\text{CN}) \\ \text{H} \end{array} \right\} \text{S}$ .

**Mercuric Thiocyanate.**  $\text{Hg}''(\text{CNS})_2$ .—This is a sparingly soluble white powder, obtained by precipitating a strong solution of mercuric nitrate by a soluble thiocyanate. It derives its chief interest from its reaction when heated; on heating in a test-tube or on kindling the powder it swells up enormously, giving off sulphur dioxide, mercurial vapours,

&c., and leaving a very bulky porous grey or brown mass containing melleo.

“Pharaoh’s serpents’ eggs” consist of mercuric thiocyanate.\* On treatment with hot water they yield a solution which is precipitated yellow by caustic alkali. On filtering the precipitated  $\text{HgO}$ , the filtrate gives the reactions of a thiocyanate after being acidulated with dilute nitric acid.

**Potassium Thiocyanate.**  $\text{KCNS} = \left. \begin{matrix} \text{CN} \\ \text{K} \end{matrix} \right\} \text{S}$ .—This substance results from the action of free sulphur or certain metallic sulphides on cyanide or ferrocyanide of potassium at a high temperature. It may also be obtained by boiling solution of potassium cyanide with sulphur, and by several other reactions.

The salt crystallises in colourless, anhydrous, deliquescent needles, very soluble in water and alcohol. The aqueous solution gradually decomposes at ordinary temperatures and more rapidly when boiled, with evolution of ammonia. The solution dissolves argentic chloride, cyanide, and thiocyanate.

On distillation with dilute sulphuric acid, potassium thiocyanate yields thiocyanic (hydrosulphocyanic) acid ( $\text{HCNS}$ ), as a liquid of a pungent odour. Part of the acid is decomposed in a manner analogous to cyanic acid, thus:  $2\text{HCNS} + 2\text{H}_2\text{O} = 2\text{H}_3\text{N} + \text{CS}_2 + \text{CO}_2$ . Another portion is split up as follows:  $3\text{HCNS} = \text{HCN} + \text{H}_2\text{C}_2\text{N}_2\text{S}_3$ .

Nitric acid and chlorine precipitate yellow per-thiocyanogen,  $\text{C}_3\text{HN}_3\text{S}_3$ , from a hot solution of potassium thiocyanate.

The following reactions of analytical interest are also given by a solution of potassium thiocyanate:—

1. Nitrate of silver precipitates white curdy argentic thiocyanate,  $\text{AgCNS}$ , insoluble in dilute nitric acid, but soluble in ammonia or soluble thiocyanates.

\* *Watts’ Dictionary* erroneously describes them as the mercurous salt. Several cases of poisoning have occurred owing to children swallowing “Pharaoh’s serpents’ eggs.”

2. Cupric sulphate produces no immediate change in a weak solution, but in a strong solution precipitates black cupric thiocyanate,  $\text{Cu}''(\text{CNS})_2$ , which turns white on standing. If sulphite of sodium or sulphurous acid be added in addition to the cupric solution an immediate white precipitate results, consisting of cuprous thiocyanate,  $\text{Cu}'\text{CNS}$ . The precipitate is insoluble in dilute sulphuric and hydrochloric acids, but dissolves in ammonia.

3. Ferrous sulphate, if quite free from ferric salt, occasions no change.

4. Ferric sulphate or chloride produces a deep red coloration, owing to the formation of soluble red ferric thiocyanate  $\text{Fe}(\text{CNS})_3$ . This is a most delicate and characteristic reaction for ferric salts and thiocyanates. The colour is not destroyed by boiling, or by cold dilute mineral acids (distinction from acetates and formates). Alkalies and ammonia precipitate brown oxide of iron, and thus destroy the colour. The colour is instantly destroyed by mercuric chloride (distinction from meconates) or by excess of argentic nitrate (distinction from formates and acetates). In presence of ferrocyanide, excess of ferric solution should be added and the liquid filtered from the precipitate of Prussian blue, when the red colour will become apparent. In presence of ferricyanide, the dark-coloured solution should be largely diluted; or the liquid may be shaken with ether, which dissolves the ferric thiocyanate and on rising to the surface will be found to be coloured red. Ferric thiocyanate may be completely removed from its aqueous solution by shaking with ether.

5. A solution of molybdic acid or molybdate of ammonium in hydrochloric acid gives a red colour with a thiocyanate which, like the similar colour produced by ferric salts, is removed from its aqueous solution by agitation with ether.

6. When treated with zinc and hydrochloric acid, sulphuretted hydrogen is evolved (which will blacken lead paper

held over the tube), and methyl-amine,  $(\text{CH}_3)_2\text{NH}$ , is formed in the solution.

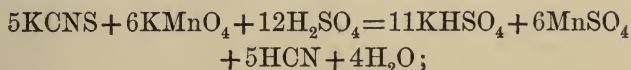
7. In a solution of a thiocyanate acidulated by dilute sulphuric acid, permanganate is instantly decolorised with formation of hydrocyanic and sulphuric acids.

Various kinds of organic matter give a red colour with soluble thiocyanates; whether the effect is due to the presence of traces of ferric compounds is not very clear.

THE DETERMINATION OF THIOCYANATES is readily effected by the following methods:—

1. Any sulphate is removed by treating the cold solution with dilute hydrochloric acid and excess of chloride of barium. The filtrate is treated with a slight excess of permanganate, and more barium chloride is added if necessary. 233 parts of  $\text{BaSO}_4$  precipitated represent 58 of thiocyanogen, CNS. The method is applicable to all thiocyanates soluble in water or dilute acids. It is interfered with by sulphites, thiosulphates and sulphides. The last class of salts may be previously removed by a solution of cadmium.

2. In the absence of other reducing agents thiocyanates may be directly titrated with dilute sulphuric acid and standard permanganate. The reaction is



or more simply,  $\text{KCNS} + \text{O}_3 = \text{KCN} + \text{SO}_3$ .

Each c.c. of decinormal permanganate decolorised represents .00193 grammes of CNS.

3. The solution is acidified with nitric acid (well boiled to free it from nitrous acid), and solution of ferric sulphate added. This produces a deep red solution of ferric thiocyanate. Decinormal silver solution is next added from a burette until the red colour is replaced by a light brown and the latter is at last destroyed. The end-reaction is better observed by adding excess of silver solution and titrating back with standard



thiocyanate until a light brown tint is permanent on agitation. Each c.c. of decinormal nitrate of silver used represents '0058 grammes of CNS. In presence of ferrocyanide, excess of iron solution must be added and the liquid filtered before titrating with nitrate of silver. The same plan is applicable in presence of ferricyanide if ferrous sulphate be substituted for the ferric salt. Cyanide may also be removed by ferrous and ferric salts and alkali, with subsequent acidification by dilute nitric acid, followed by filtration. Sulphides may also be removed by filtering the solution *after* addition of iron salts and alkali, but *before* adding nitric acid. In presence of chlorides, bromides, or iodides, the process is still available, if, after the termination of the reaction, the silver precipitate be filtered off and treated in the following manner:—The silver compound is dried and mixed with a large excess of pure sodium carbonate. The mixture is added gradually to fused nitre contained in a porcelain crucible. When the action is complete, the cooled mass is dissolved in water, filtered, and neutralised by dilute nitric acid, and titrated with standard nitrate of silver, using neutral chromate as an indicator. The quantity of silver solution used represents the chloride, bromide, and iodide present. Its volume, deducted from the amount originally required, represents the silver corresponding to the thiocyanate. The thiocyanate may also be determined by estimating the sulphate formed on fusion by acidulating with hydrochloric acid and adding barium chloride. This plan does not necessitate the previous removal of cyanides, ferro-, or ferricyanides.

4. Any sulphide, cyanide, ferro-, or ferri-cyanide is separated by iron salts, as in process 3, but the liquid is rendered slightly acid with hydrochloric instead of nitric acid. The solution is then treated with sulphite of sodium and a solution of cupric sulphate added. Phosphates and other inorganic salts forming insoluble copper compounds may be got rid of by digesting the precipitate with cold dilute hydrochloric acid. The white pre-

precipitate of cuprous thiocyanate is filtered off, washed, dried at 100° C. and weighed. 121.3 parts of  $\text{CuCNS}$  represent 58 of thiocyanogen. The process is not affected by bromides or chlorides, but is not directly applicable in presence of iodides, which are precipitated as white cuprous iodide.

5. Very small quantities of thiocyanates, such as are met with in soda-lyes, may be determined by acidifying the lye with hydrochloric acid, and adding zinc chloride. The ferrocyanide of zinc is filtered off, and the filtrate coloured by ferric chloride. The tint is then compared colorimetrically with that produced by a known quantity of thiocyanate treated similarly.

6. INSOLUBLE THIOCYANATES may be fused with alkaline carbonate and nitre, as in process 3, the sulphate produced being determined by precipitation with barium chloride. They may also be decomposed by sulphuretted hydrogen, the liquid filtered, ammoniacal solution of copper added, the sulphide of copper filtered off, and the filtrate treated with dilute sulphuric acid and sodium sulphite, when cuprous thiocyanate will be obtained as in process 4.

7. To determine the metals in thiocyanates, the salts may be decomposed by sulphuric acid as described on page 37.

**Potassium Iso-Thiocyanate.** Potassium thiocarbimide.

$\left. \begin{matrix} \text{CS} \\ \text{K} \end{matrix} \right\} \text{N}$ .—This isomer of the ordinary thiocyanate is the type of a series of salts which differ from the true thiocyanates in many reactions. Thus, the silver salt is light yellow, and but slightly soluble in ammonia. With zinc chloride, thiocyanates give no reaction, but the isomeric salts give a voluminous deep-yellow precipitate, and with neutral ferric chloride a brown coloration, disappearing on adding excess of the iron salt. Cupric sulphate gives a greenish yellow precipitate.

Potassium iso-thiocyanate is partly converted into the normal salt by repeatedly evaporating its solution, and completely so by fusion.

## ALCOHOLS.

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THE term "alcohol" is popularly applied to the pure essence or spirit which imparts to wine or unfermented liquids an intoxicating property. When used without qualification and as a proper name, it is to be understood as applying to ethyl-alcohol or spirit of wine.

In modern chemistry the word alcohol, in a generic sense, has a much wider meaning, being applied to a very numerous class of bodies, many members of which present a close resemblance to spirit of wine, while in others the properties which are characteristic of ordinary alcohol are conspicuous by their absence.

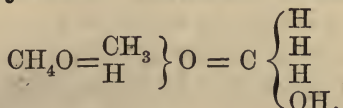
AN ALCOHOL may be defined as a neutral compound of carbon, hydrogen, and oxygen, capable of reacting directly on acids with elimination of water and formation of ethers.

The only alcohols which will be fully described in this work are—

$\text{CH}_3\text{OH}$ . Methyl Alcohol, occurring in wood spirit;  
 $\text{C}_2\text{H}_5\text{OH}$ . Ethyl Alcohol, occurring in spirit of wine;  
 $\text{C}_5\text{H}_{11}\text{OH}$ . Amyl Alcohol, occurring in potato spirit; and  
 $\text{C}_3\text{H}_5'''(\text{OH})_3$ . Glycerin, obtained by the decomposition of fats.

Carbolic and cresylic acids, which are sometimes regarded as phenyl and cresyl alcohols, are described fully in the sections referring to them.

Sodium ethylate, which is sometimes spoken of as sodium alcohol, is referred to on page 78.

**METHYL ALCOHOL.****Methylic Hydrate. Carbinol. Wood-spirit.**

Pure methyl alcohol is a colourless mobile liquid of purely spirituous odour. (The empyreumatic odour of common wood-spirit is due to impurities.) The boiling point is about 66° C., but varies not inconsiderably with the nature of the containing vessel.\* Methyl alcohol is miscible in all proportions with water, ordinary alcohol, or ether, and possesses considerable solvent properties. In its chemical reactions it presents close analogies to ethylic alcohol (see page 77). By the oxidation of methyl alcohol, formic acid is produced.

Pure methyl alcohol may be obtained by distilling 1 part of purified commercial wood-spirit with 1 of sulphuric acid and 2 of acid oxalate of potassium. The receiver is changed as soon as crystals of methyl oxalate begin to form in the neck of the retort. The process is then continued till the temperature of the mixture reaches about 170° C. The crystals of methyl oxalate are dried by pressure, treated with water, allowed to stand some time, and then redistilled, when pure dilute methyl alcohol is obtained, which may be rectified over quicklime or baryta. According to Dumas and Mitscherlich the density of absolute methyl alcohol is ·8142 at 0° C., and ·7980 at 20° C. This would give a density of ·8061 at 10° C., which closely corresponds with the independent result of Deville, who obtained ·8070 as the density at 10° C. The mean of these results gives a calculated density of ·8021 at 15·5° C. (=60° F.) Dupré's figures are very sensibly different. Duclaux, who recently experimented on a very pure product, obtained ·7995 as the density of methyl alcohol at 15° C.† It is doubtful,

\* The statements respecting the boiling point of pure methyl alcohol exhibit great discrepancies. Dupré gives it as 58·6° C.

† The boiling point was exactly 66° C., and each fraction distilled had precisely the same surface tension (*Annales Chim. et Phys.* 1878, xiii. 86).



however, whether water at 15° C., at 4° C., or at 0° C. was taken as unity. Ure is the only investigator who has compiled a detailed table of the densities of mixtures of methylic alcohol and water. If the true density of methyl alcohol at 15·5° C. be taken as ·8021, Ure's absolute spirit contained 2·2 per cent. of water. Hence, in using the following table (Ure's), the percentage of methyl alcohol found should be multiplied by ·978 to obtain the true result.

PERCENTAGE BY WEIGHT OF ABSOLUTE METHYL ALCOHOL  
Contained in wood-spirit of different gravities at 60° F. (= 15·5° C.)

Specific Gravity.	Percentage of Methyl Alcohol.	Specific Gravity.	Percentage of Methyl Alcohol.	Specific Gravity.	Percentage of Methyl Alcohol.	Specific Gravity.	Percentage of Methyl Alcohol.
·8136	100·00	·8674	82·00	·9008	69·44	·9344	53·70
·8216	98·11	·8712	80·64	·9032	68·50	·9386	51·54
·8256	96·11	·8742	79·36	·9060	67·57	·9414	50·00
·8320	94·34	·8784	78·13	·9070	66·66	·9448	47·62
·8384	92·22	·8822	77·90	·9116	65·00	·9484	46·92
·8418	90·90	·8842	75·76	·9154	63·30	·9518	43·48
·8470	88·30	·8876	74·63	·9184	61·73	·9540	41·66
·8514	87·72	·8918	73·53	·9218	60·24	·9564	40·00
·8564	86·20	·8930	72·46	·9242	58·82	·9584	38·46
·8596	84·75	·8950	71·43	·9266	57·63	·9600	37·11
·8642	83·33	·8984	70·42	·9296	56·18	·9620	35·71

Methyl alcohol occurs among the products of the dry distillation of wood, the aqueous portion of which generally contains about 1 per cent. of the alcohol. The watery liquid is separated from the tar and distilled. The first portion of the distillate is again rectified over slaked lime to remove acid, &c., the product treated with sulphuric acid to remove tar and neutralise ammonia and methylamine, and the liquid redistilled and rectified once or more over quicklime.

The liquid thus obtained is known as—

### **Wood-spirit. Wood-naphtha. Pyroxilic Spirit.**

*French*—Esprit de Bois. *German*—Holzgeist.

This is a very complex liquid, containing variable quantities of methyl alcohol, acetone, acetate of methyl, dimethyl-acetal,

water, &c. The following table shows the composition, densities, and boiling points of these bodies:—

	Specific Gravity.	Boiling Point. ° C.
Methyl alcohol, $\text{CH}_4\text{O} = \left( \begin{smallmatrix} \text{CH}_3 \\ \text{H} \end{smallmatrix} \right) \text{O}$	·8142 (·8021 at 15·5° C.)	66·0
Methyl acetate, $\text{C}_3\text{H}_6\text{O}_2 = \left( \begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_3\text{O} \end{smallmatrix} \right) \text{O}$	·9562	56·3
Acetone, $\text{C}_3\text{H}_6\text{O}_2 = \left( \begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_3\text{O} \end{smallmatrix} \right)$	·8140 (at 18° C.)	56·3
Dimethyl-acetal, $\text{C}_4\text{H}_{10}\text{O}_2 = \left( \begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_4 \end{smallmatrix} \right)_2 \text{O}_2$	·8555	65·0

The methylic alcohol contained in wood spirit can be separated in a state of tolerable purity by saturating the liquid with fused chloride of calcium, which combines with the methyl alcohol to form a compound of the formula  $\text{CaCl}_2, 2\text{CH}_4\text{O}$ , which is not decomposed at a temperature of 100° C. The mixture is, therefore, heated on the water-bath, by which the acetone and other constituents of the wood-spirit are driven off and may be collected if desired. The residue is next distilled with water, when the compound of chloride of calcium and methyl alcohol is decomposed and the latter distils over; and may, if required, be rectified from quicklime in the same way as ordinary alcohol.

The density of crude wood-spirit is not a certain indication of the proportion of methyl alcohol present, as its composition varies considerably. For dissolving resins, especially gum sandarac and mastic, painters choose naphtha holding some of the essential oils in solution. By treating crude wood-spirit with lime, and again distilling, a product of low specific gravity is obtained containing little acetone and much methyl alcohol, but the menstruum for dissolving resins is prepared by distilling off the refined portion of the crude naphtha without employing lime. The former product has a low gravity and is miscible with water, but the latter is heavier, contains much acetone,\* and becomes milky on dilution from the separation of empyreumatic oils.

\* For further information respecting acetone, see page 70.

Wood-naphtha is quite unfit for use as a beverage, being nauseous and highly deleterious. Pure methyl alcohol is free from these objections.

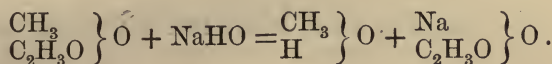
Commercial wood-spirit gives a brown coloration on heating with caustic alkali. Mixed with concentrated sulphuric acid, a reddish or reddish-brown colour is developed. The smell of wood-spirit is very characteristic.

ASSAY OF WOOD-SPIRIT.—The proportion of real methyl alcohol in commercial wood-spirit is best estimated by the following process, devised by G. Krell :—Into a dry flask holding about 100 c.c., 30 grammes of phosphorus di-iodide are introduced. The flask is closed with a doubly perforated cork or glass stopper. One orifice is fitted with a small tap-burette or funnel, in which 5 c.c. of the wood-spirit (measured at  $15^{\circ}\text{C.} = 59^{\circ}\text{F.}$ ) are placed. In the other orifice, a condensing tube, bent at an obtuse angle, is fitted. The wood-spirit is then allowed to enter drop by drop, and, when all is introduced, the flask is heated for five minutes in boiling water and then inclined to distil off the methyl iodide which has been formed. At the close of the operation, a current of air is passed into the apparatus, through the funnel, to drive over any vapour of methylic iodide.

The distillate is collected in a graduated glass tube holding 25 c.c. When the distillation is finished, the condenser is rinsed out with water into the receiver, the contents of which are well shaken, and the methyl iodide allowed to settle, when the volume of it is read off. 5 c.c. of pure anhydrous methyl alcohol yield under these conditions 7.45 c.c.\* of the iodide. Any methyl acetate present in the sample is by this process converted into iodide, and thus increases the apparent percentage of methyl alcohol. For most purposes the error thus introduced can be neglected. If desired, the quantity present can be previously determined approximately by heating a known

\* The deficiency appears to be due to the formation of trimethyl-phosphine  $(\text{CH}_3)_3\text{P}$ .

quantity of the wood-spirit with standard soda, and titrating the excess with standard acid. The quantity of soda neutralised by the methyl acetate is represented by the equation,



Consequently, 40 parts of NaHO neutralised correspond to 104 of methyl acetate, or 42 of methyl alcohol. The amount of methyl alcohol so found should be subtracted from the total amount corresponding to the iodide, in order to ascertain the real amount of methyl alcohol existing as such in the sample.

The other constituents of wood-spirit when treated with iodide of phosphorus yield distillates soluble in water, or are converted into resinous bodies, with the exception of dimethyl-acetal, 5 c.c. of which yields 5·3 c.c. of methyl iodide.\*

For the preparation of the iodide of phosphorus, 15·5 grammes of phosphorus are dissolved in 350 c.c. of carbon disulphide, and 127 grammes of iodine are gradually added, the vessel being kept well cooled. The di-iodide separates in crystals, which are dried in a slightly warm current of air, and preserved in a well stoppered bottle.

Grodski and Krämer used 15 grammes instead of 30 of the di-iodide, and, after dropping in the 5 c.c. of wood-spirit, allowed a solution of iodine in an equal weight of hydriodic acid of 1·7 sp. gr. to flow in. By this process these chemists obtained results agreeing fairly with theory.

The detection of small admixtures of ethyl alcohol in wood-spirit is less important than the converse. The following tests have been proposed for the purpose.

1. M. Berthelot heats the sample with twice its volume of concentrated sulphuric acid. If 1 per cent. of ethyl alcohol be present, ethylene is evolved, and may be absorbed by bromine and estimated as  $\text{C}_2\text{H}_4\text{Br}_2$ . Acetone and the normal

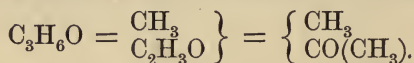
\* *Journ. Chem. Soc.* 1877, ii. 229.



impurities of wood-spirit may yield CO and CO<sub>2</sub>, but not ethylene.

2. Another very delicate test is based on the fact that ethyl alcohol forms iodoform when treated with iodine in presence of an alkali—a reaction which is not common to pure methyl alcohol. As, however, acetone and many other bodies act in the same way as ordinary alcohol, the test becomes practically one for the purity of methyl alcohol, rather than for the detection of ethyl alcohol in the commercial product.

**Acetone.** Acetic Ketone. Pyro-acetic spirit.



Acetone occurs largely in some varieties of wood-spirit, and is a constant product of the dry distillation of acetates. It is also obtained from the residue left after manufacturing aniline by the distillation of nitrobenzene with acetic acid and iron. Acetone is a colourless limpid liquid of peculiar ethereal odour and burning taste. It is miscible in all proportions with ether, alcohol, and water. It dissolves nearly all resins, gums, camphor, and fats. Gun-cotton dissolves in it with facility. Caustic potash and dry calcium chloride are insoluble in acetone. This fact distinguishes acetone from methyl alcohol. The presence of much acetone in wood-naphtha is detected by mixing the sample with twice its measure of a *saturated* aqueous solution of calcium chloride, when the acetone will be separated, and form a layer at the surface of the liquid. The test becomes more delicate if, instead of employing a solution, *powdered* calcium chloride be added to the naphtha.

A more delicate reaction is that of J. E. Reynolds described on page 71, the success of the test for the detection of wood-spirit depending on the presence of acetone in the latter.

**Methylated Spirits of Wine** is a mixture of 90 per cent. of rectified spirit (ethyl alcohol) with 10 per cent. of commercial wood-spirit. The acetone and other constituents of the wood-

naphtha are so difficult to remove that the spirit is considered to be permanently unfitted for drinking purposes, and therefore is not subject to duty.\*

As methyl alcohol has a sensibly lower boiling point than ethyl alcohol, methylated spirit boils at an intermediate temperature—a circumstance which may be utilised for the approximate determination of the proportion of wood-spirit contained in it. For the following data we are indebted to Dr Ure.

				Boiling Point.	
				°C.	°F.
Wood-spirit	.	.	·870	62·2	144
"	.	.	·832	60·0	140
Alcohol	.	.	·870	82·2	180
"	.	.	·832	77·2	171·1

An addition of 10 per cent. of wood-naphtha to alcohol lowers the boiling point 3·3° C. (=6° F).

**Detection of Methyl Compounds in Alcoholic Liquids.**—In consequence of the cheapness of methylated spirit as compared with pure ethyl alcohol, there is a great inducement to substitute the former in tinctures and other preparations which should only contain the latter. On this account it is frequently important to test alcohol for any admixture of wood-spirit, and various methods have been devised for the purpose,—some founded on the detection of methyl alcohol itself, and others on the recognition of the acetone, which appears to be constantly present in commercial wood-spirit.

1. The following process for testing alcohol depends on the presence of acetone, and was devised by J. E. Reynolds:—“Take 200 c.c. of the spirit, and rapidly distil off 50 c.c.; dilute the distillate with an equal volume of water, and slightly warm with addition of a few c.c. of solution of potassium

\* By rendering methylated spirit absolute, the impurities are so far removed that the resultant alcohol is not wholly disqualified for drinking use, and hence the Excise have recently disallowed the sale of absolute methylated alcohol.

hydrate. On cautious addition of mercuric chloride, the oxide at first thrown down is speedily redissolved; excess of the mercuric salt must be carefully avoided. The alkaline liquid should be filtered clear, much of the alcohol allowed to evaporate slowly, and the residue then divided in two portions. One part is to be violently boiled for a few minutes; a yellowish white, gelatinous precipitate will suddenly make its appearance if the acetone compound be present. In the second portion, dilute acetic acid, when added in excess, should produce a bulky, white, gelatinous precipitate, containing, when washed and completely dried, between 78 and 79 per cent. of mercury."

2. The following process has been devised by MM. Riche and Bardy for the detection of methyl alcohol in commercial spirit of wine. It depends on the formation of methyl-aniline-violet. 10 c.c. of the sample of alcohol, previously rectified if necessary over potassium carbonate, are placed in a small flask with 15 grammes of iodine, and 2 grammes of red phosphorus. Methyl and ethyl iodides are formed, and should be distilled off into about 30 c.c. of water. The heavy oily liquid which settles to the bottom is removed with a pipette, and collected in a flask containing 5 c.c. of aniline. The flask should be placed in cold water, in case the action should be violent. If necessary, it may be stimulated by gently warming the flask. After one hour the product is boiled with water, and solution of soda added, when the bases rise to the top as an oily layer, which may be drawn off with a pipette after filling the flask with water up to the neck. 1 c.c. of the oily liquid thus obtained is next oxidised by adding it to 10 grammes of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate. After being thoroughly mixed, the whole is introduced into a glass tube and heated to 90° C. for eight or ten hours. The product is exhausted with warm alcohol, the liquid filtered, and made up with alcohol to 100 c.c. If the sample of alcohol were pure, the tint of the liquid is red, but in presence of 1 per cent. of methyl alcohol, it has a distinct

violet shade ; with  $2\frac{1}{2}$  per cent. the shade is very distinct, and still more so with 5 per cent. To detect more minute quantities of methyl alcohol, 5 c.c. of the coloured liquid are diluted to 100 c.c. with water, and 5 c.c. of this again diluted to 400 c.c. The liquid thus obtained is heated in porcelain, and a fragment of white merino (free from sulphur) immersed in it for half an hour. If the alcohol were pure the wool will remain white ; but if methylated, the fibre will become violet.

3. The following is the process of Mr J. T. Miller for the detection of methyl alcohol in spirituous liquids. In the case of tinctures and other liquids containing fixed matters, the greater part of the spirit must be distilled off and the test applied to the distillate. The process depends on the fact that methyl alcohol forms formic acid when treated with oxidising agents, but that ethyl alcohol yields a mere trace of the same body. Nevertheless, the fact that a trace of formic acid (or other reducing agent) is formed must not be overlooked.

"Into a small flask or test-tube having a long bent tube attached put 30 grains of powdered red chromate of potassium, half an ounce of water, 25 minims of strong sulphuric acid, and 30 or 40 minims of the spirit to be tested. Set the mixture aside for a quarter of an hour and then distil half a fluid ounce. Place the distillate in a small dish, add a very slight excess of carbonate of sodium, boil down to about a quarter of an ounce, add enough acetic acid to impart a distinct but feeble acid reaction, pour the liquid into a test-tube, add a grain of nitrate of silver dissolved in about 30 drops of water, and heat gently for a couple of minutes. If the liquid then merely darkens a little, but continues quite translucent, the spirit is free from methylic alcohol ; but if a copious precipitate of dark-brown or black metallic silver separates, and the tube, after being rinsed out and filled with clean water, has a distinct film of silver, which appears brown by transmitted light (best seen by holding it against white paper), the spirit is methylated."\*

\* *Attfield's Chemistry.*



The accurate determination of methyl alcohol in presence of ethyl alcohol is very difficult. Dupré has described the following method of detecting methyl alcohol in spirituous liquids, and approximately estimating the amount.

Five ounces of the spirit are distilled twice, having been rendered alkaline the first and acid the second time, about two-thirds being passed over each time. The distillate is next shaken with dry potassium carbonate, and allowed to stand twelve hours. The upper layer is then removed with a pipette, and again twice distilled, about half an ounce being driven over each time. This last half-ounce will contain any methylic alcohol present in the original five ounces of the sample.

All the distillations should be conducted in an apparatus having all the parts air-tight, expansion of the contained air being allowed for by a mercury valve. In this way the distillation can be effected without loss. About one-third of the last distillate is next diluted with about six times its measure of water, and in this spirituous liquid the alcohol is carefully determined, first by the density (see page 82), and subsequently by oxidation to acetic acid, with volumetric estimation of the latter (see page 92). With pure alcohol both methods should give results agreeing within 0.1 per cent. In presence of methyl alcohol, the oxidation method gives a sensibly lower result, as no fixed acid is formed by its oxidation. If any appreciable quantity of methyl alcohol be present, on opening the flask in which the oxidation is performed, a slight escape of gas will take place, owing to the carbon dioxide produced. With pure ethyl alcohol, on the contrary, a partial vacuum is formed. In a whisky to which 10 per cent. of methylated spirit was added, the specific gravity method gave 10.08 per cent. of alcohol in the diluted distillate, against 9.50 per cent. by the chromic acid method. A determination of the alcohol by Geissler's vaporimeter affords a useful check. Thus, the same whisky above mentioned gave 10.45 per cent. of alcohol by this process, owing to the presence of methyl alcohol increasing

the tension of the vapour.\* The remainder of the distillate in which the methyl alcohol has been concentrated may be examined for that body by the chemical tests (see page 71, *et seq.*).

A process has been described by Hager for determining the proportions of methylic and ethylic alcohols existing in a mixture, by converting them into the corresponding oxalates by distillation with potassium oxalate and strong sulphuric acid. The methyl oxalate,  $(\text{CH}_3)_2\text{C}_2\text{O}_4$ , so obtained is a solid crystalline body, while the ethyl oxalate,  $(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4$ , is a liquid. Although, when in an unmixed state, mere traces of methyl alcohol can be detected by the above reaction, the presence of ethyl alcohol in the sample, and, consequently, of ethyl oxalate in the product of distillation, renders the method useless, as the crystalline methyl oxalate remains dissolved in the homologous liquid ether. Methyl oxalate, however, is soluble in water, while ethyl oxalate is practically insoluble. Hence, by shaking the distillate with water, and determining the oxalic acid produced by its treatment with caustic alkali, it was thought possible that a practical process might be obtained. The experiments made by the author in this direction ended in complete failure, very considerable quantities of ethylic oxalate always passing into the aqueous solution, although care was taken not to leave the oily layer in contact with the water for any length of time.

From some recent researches on the surface tensions of the alcohols by M. Duclaux,† it appears extremely probable that methyl alcohol could be detected, and even approximately determined, in spirituous liquids by simply noting the number of drops of the sample delivered by a pipette constructed to deliver 100 of water. A liquid containing 20 per cent. by volume of ethylic alcohol will give 176 drops, while methylic alcohol of the same strength will give only 147·5 drops.

\* *Analyst*, i. 4.

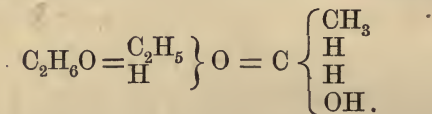
† *Annales Chim. et Phys.* [5], xiii. 76, *et seq.*

**ETHYL ALCOHOL.**

**Alcohol. Ethylic Hydrate. Methyl Carbinol. Spirit of Wine.**

*French*—Alcool.

*German*—Weingeist.



Ethyl alcohol is the pure essence or spirit which imparts to wine and other fermented liquids an intoxicating property. When used without qualification, and as a proper name, the term *alcohol* is to be understood as applying to ethyl alcohol, or “spirit of wine.”

Pure anhydrous or “absolute” ethyl alcohol is a limpid, colourless liquid, of a penetrating and agreeable odour and hot pungent taste. It boils at 78·4° C. (= 173·1° F.) It has never been frozen. Absolute alcohol has a density of ·79381 at a temperature of 15·5° C. (= 60° F.), and expands rapidly by increase of temperature.

Absolute alcohol burns with a whitish flame, which deposits carbon on a cold surface held in it. If the alcohol contain water, the flame produced is quite blue.

Alcohol volatilises rapidly at ordinary temperatures.

Alcohol is miscible with water in all proportions, a considerable evolution of heat and contraction in bulk taking place on admixture. The whole of the water can be removed from it with great difficulty only; even repeated distillation does not remove the last 10 per cent. (sp. gr. ·8228).

The strongest alcohol producible by distillation is known as rectified spirit of wine. The British Pharmacopœia describes this as containing 84 per cent. of real alcohol, and having a density of ·838. By repeated treatment with carbonate of potassium or quicklime, with subsequent distillation, the last traces of water may be removed from alcohol, which is then said to be “absolute.” In commerce

several different strengths of absolute alcohol are recognised, the term being applied to any stronger spirit than can be obtained by mere distillation.

Absolute or very strong alcohol is powerfully poisonous, destroying the vital functions of the tissues by abstracting their moisture. For a similar reason, strong alcohol is a powerful antiseptic.

Alcohol absorbs many gases with considerable avidity. Some of them, such as hydrochloric and nitrous acids, decompose it with formation of the corresponding ethers (ethyl chloride,  $C_2H_5Cl$ , and ethyl nitrite,  $C_2H_5NO_2$ ).

Alcohol is a powerful solvent for fluid and solid bodies, dissolving resins, volatile oils, camphor, phenol, creasote, glycerin, and numerous salts, acids, and organic bases. As a rule, the metallic chlorides, bromides, iodides, acetates, &c., are soluble in alcohol; while the carbonates, borates, sulphates, phosphates, oxalates, tartrates, malates, &c., are insoluble.\*

Sulphur and phosphorus are slightly soluble in alcohol. Iodine is readily soluble with brown colour; on addition of alkali the liquid is decolorised with formation of iodoform.

Bromine and chlorine act on absolute alcohol by removing part of the hydrogen and forming substitution products (chiefly bromal and chloral).

Concentrated nitric and chloric acids act very violently on alcohol, forming aldehyde, acetic acid, and other products. Chromic acid and permanganate of potassium react similarly.

Sulphuric, arsenic, and phosphoric acids react on alcohol, with production of ethyl-acids. When the liquid is heated, ethylene gas or ordinary ether results, according to the boiling point of the liquid. Acetic, formic, oxalic, hydrochloric, and other acids decompose absolute alcohol with formation of the corresponding ethers.

\* Most deliquescent salts, except potassium carbonate, are soluble in alcohol. Inorganic compounds which are insoluble or sparingly soluble in water are also insoluble in alcohol.



Potassium and sodium dissolve in absolute alcohol, forming potassium and sodium ethylates ( $\text{C}_2\text{H}_5\text{KO}$  and  $\text{C}_2\text{H}_5\text{NaO}$ ), which are decomposed by water into alcohol and caustic alkalies. Dr Richardson has recently proposed to employ an alcoholic solution of sodium ethylate as a caustic.

**Examination of Commercial Alcohol.**—Ordinary spirit of wine is commonly assumed to consist of pure ethylic alcohol, more or less mixed with water. This, however, is frequently far from true, commercial ethylic alcohol often containing distinct traces of higher homologues, of aldehyde and acetic acid, of volatile oils, and of various fixed impurities, both organic and inorganic. Methylated spirit of wine is an acknowledged mixture of ethyl alcohol and wood spirit. For the detection of the latter body in alcoholic liquids in which its unacknowledged presence is suspected, see the section on methyl alcohol, page 71, *et seq.*

The other common impurities of commercial alcohol may be detected in the following manner:—

**FIXED IMPURITIES** may be detected and estimated by evaporating to dryness 50 or 100 c.c. of the spirit, and weighing the residue, if any. The proportion of inorganic matter can be ascertained by igniting the residue carefully at a low red heat. Some idea of the nature of the organic matter may be obtained by smelling the fumes produced when the residue is first heated.

**OILY AND RESINOUS MATTERS** may be detected by diluting the spirit somewhat largely, when they are precipitated, and impart a milky appearance to the liquid.

**ACETIC ACID** will be indicated by the acid reaction of the spirit.

**ALDEHYDE** imparts a peculiar flavour to the spirit. When present in quantity the spirit becomes brown when heated with caustic alkali. A smaller quantity is detected by adding a few drops of solution of argentic nitrate, and exposing the

liquid to a good light for twenty-four hours, when the silver will be reduced and deposited as a black powder if aldehyde or other reducing agent be present. Traces of aldehyde, &c., are nearly always present in commercial samples of alcohol. The "British Pharmacopœia" directs the silver test to be made by adding 30 fluid grains (2 c.c.) of decinormal argentic nitrate to 4 fluid ounces of the sample to be tested. After exposure to the light for twenty-four hours, and decantation from the black precipitate, no further reduction of silver should occur on repeating the treatment. A negative result on adding more silver solution and again exposing the liquid to light, proves the absence of a greater proportion of reducing agents per pint of spirit than can decompose about  $2\frac{1}{2}$  grains of nitrate of silver.

AMYLIC ALCOHOL may be searched for by the methods described on page 119, *et seq.*

**Detection of Alcohol.**—When tolerably concentrated, alcohol is readily recognised by its physical properties, after previous distillation if necessary.

In a dilute state, the following tests for alcohol are of service:—

1. Berthelot's test depends on the formation and properties of ethyl benzoate (benzoic ether). The sample of liquid is shaken in the cold with a few drops of benzoyl chloride. This is not readily acted on by cold water; but, in presence of alcohol, ethyl benzoate is formed, which remains mixed with the excess of benzoyl chloride. This is removed from the bottom of the liquid with a pipette, and a drop or two of it heated with a solution of caustic potash or soda. This dissolves the benzoyl chloride immediately, without acting at first on the benzoic ether. The latter is nearly insoluble in water, has a pleasant aromatic odour, and burns with a brilliant smoky flame. It boils at  $213^{\circ}\text{C}$ . With 20 c.c. of a liquid containing 1 per cent. of alcohol, M. Berthelot found the reaction very distinct, and with .1 per cent. the test answers if

sufficient of the liquid be used. In presence of foreign matters of strong odour the method is quite useless.

2. Mr J. Hardy detects small quantities (1 per cent.) of alcohol in aqueous liquids by shaking the sample for a few minutes with a small quantity of powdered guaiacum resin taken from the interior of a lump. The liquid is filtered, and few drops of hydrocyanic acid and a drop of weak solution of sulphate of copper added. In presence of alcohol a blue colour is produced, far more intense than is due to the slight colour of the solution of copper. When the alcohol is present in but small quantity, the tube should be viewed over white paper, and a blank experiment with distilled water made side by side with the sample. The author has verified this test.

3. E. W. Davy detects 0.1 per cent. of alcohol in water by adding a few drops of the liquid cautiously to a solution of 1 part of molybdic acid in 10 of strong sulphuric acid gently warmed in a porcelain capsule. A blue coloration appears immediately, or after a few moments. Other alcohols, ether, and aldehyde give the same reaction, but chloroform and chloral hydrate do not. The author has proved the delicacy of this test to the above-named extent.

4. Riche and Bary use a reaction dependent on the production of aldehyde from ethylic alcohol by oxidising agents, and the reaction of aldehyde, methylal, acetal, &c., on salts of rosaniline.\*

5. A very delicate test for small quantities of alcohol is that of Lieben, as modified by Hager.† It depends on the fact that alcohol under the influence of iodine and an alkali yields iodoform,  $\text{CHI}_3$ , the properties of which are very characteristic. To 10 c.c. of the clear suspected liquid, five or six drops of a 10 per cent. solution of caustic potash or soda are added, and the liquid is warmed to about  $50^\circ \text{C}$ . A solution of iodide of potassium, fully saturated with free iodine, is next added drop

\* *Compt. Rend.* lxxxii. 768.

† *Zeitsch. Anal. Chem.* ix. 492.

by drop with agitation, until the liquid becomes permanently yellowish brown, when it is carefully decolorised by a further cautious addition of the caustic alkali solution. If alcohol were present, iodoform is gradually deposited at the bottom of the tube in yellow crystals, which, after standing, may be examined with a lens. Under a microscopic power of 300 diameters its appearance is very characteristic, the usual forms being hexagonal plates, stars, and rosettes. Spirit diluted with 2000 parts of water, when treated as above and allowed to stand 12 hours, gives a distinct dust-like deposit of iodoform. The author has verified this test.

When chloroform and similar liquids are to be examined, 2 c.c. should be shaken with 10 c.c. of water, and the liquid passed through a wet filter, the test being applied to the filtrate.

Unfortunately, the above delicate reaction is not peculiar to alcohol, being produced also by acetone, aldehyde, propylic and butylic alcohols and aldehydes, various ethers, meconic and lactic acids, turpentine, sugar, &c. On the other hand, it is not given by pure methyl or amyl alcohol, chloroform, chloral, glycerin, or ether, nor by acetic, formic, or oxalic acid.

6. J. C. Thresh\* has recently described a method of detecting and estimating small quantities of alcohol which is based on its oxidation to aldehyde by a mixture of bichromate of potassium and dilute sulphuric acid. It is evident that excess of the oxidising mixture must be avoided, or the aldehyde will be wholly converted into acetic acid, as actually occurs in Dupré's modification of the method, as described on page 93. The inventor of the process claims that it is capable of giving approximate quantitative results with a liquid containing .04 to .40 per cent. of alcohol, and that it will detect with certainty .01 per cent. The following are the details of the method:—

100 c.c. of the dilute alcoholic liquid are placed in a small flask, together with 2 c.c. of a cold saturated solution of bichromate of potassium and 12 c.c. of normal sulphuric acid. A few

\* *Pharm. Journ.* Nov. 16, 1878, p. 408.



pieces of pumice are added to prevent bumping, a bent tube attached, and 20 c.c. distilled off slowly into a graduated tube containing 3 c.c. of a syrupy solution of caustic soda. The distillate is then heated, kept at the boiling point for a few seconds, and placed aside for two hours. If the original spirituous liquid contained  $\cdot 10$  per cent. of alcohol, the contents of the tube will have acquired a deep yellow colour and have deposited flocks of aldehyde resin; with  $\cdot 05$  per cent. no resin separates, but the fluid is deep yellow and perceptibly opalescent; with  $\cdot 01$  per cent. the colour is only just perceptible, but the characteristic odour is still very distinct. Mr Thresh employs the method colorimetrically by comparing the depth of colour with that produced by a liquid containing a known amount of aldehyde. His test experiments show that the method is approximately accurate within the limits named, and may be applied to the determination of alcohol in essential oils, urine, &c.

**Determination of Alcohol.**—The estimation of alcohol in admixture with wood-spirit, amyl alcohol, chloroform, ether, &c., may be effected by the methods described under these substances. In by far the greater number of instances the determination of alcohol is effected by separating it from fixed substances by distillation, and then ascertaining the proportion of alcohol present in the spirituous liquid condensed. This is practically the,

DETERMINATION OF ALCOHOL IN MIXTURES CONSISTING ESSENTIALLY OF ALCOHOL AND WATER ONLY.

1. This is most generally effected by accurately ascertaining the specific gravity of the mixture. From the specific gravity, the percentage of real alcohol is readily ascertained by reference to tables, on the construction of which great care has been bestowed by various observers, the subject being of great importance for Excise purposes. By the Excise, a glass or metal hydrometer is employed, the temperature of the liquid being carefully noted. In the laboratory, the specific gravity bottle

is a more satisfactory and accurate instrument. In all cases the bottle must be filled at exactly  $15.5^{\circ}\text{C.}$  ( $=60^{\circ}\text{F.}$ ), for alcohol dilating rapidly by increase of temperature, very erroneous results may be obtained if this precaution be not rigidly observed.\* Care must be taken that the bottle contains no air bubbles, and the stopper must be inserted when the liquid in the bottle (after being well stirred) shows a temperature of  $15.5^{\circ}\text{C.}$  ( $=60^{\circ}\text{F.}$ ). A bottle holding 50 c.c. is of suitable capacity for general use, but for some purposes a smaller one will be found serviceable. It should never be trusted to contain the weight of water marked on it, but should be carefully filled with water at  $15.5^{\circ}\text{C.}$  ( $=60^{\circ}\text{F.}$ ) and the weight accurately noted. The weight of the contained spirituous liquid is then in each case divided by the observed weight of contained water, the dividend being the specific gravity of the sample. It is desirable to use a bottle having a thermometer attached to the stopper, so that when the bottle is filled and the stopper inserted the thermometer will be wholly immersed in the liquid under examination. The specific gravity bottle may be conveniently replaced by the U-shaped tube described on page 6.

The proportion of alcohol contained in spirituous liquids is expressed in three ways. 1. Percentage of alcohol by weight. 2. Percentage of alcohol by volume. 3. Percentage of proof spirit. Of these, the first, in the opinion of the author, is the most satisfactory, but both the other plans serve for certain purposes. It is convenient in some cases to know the weight of alcohol in 100 measures of the spirituous liquid. The term

\* If all available water be sensibly above the standard temperature, it can readily be cooled by dissolving in it some powdered thiosulphate of sodium, the specific gravity bottle filled with spirit being immersed in the cooling liquid. When the temperature of the spirit is but a few degrees above  $15.5^{\circ}\text{C.}$ , a correction of the observed density may be made according to the following formula, in which  $D$  is the required density at  $15.5^{\circ}\text{C.}$ ,  $D'$  the observed density, and  $d$  the difference in temperature between  $15.5^{\circ}\text{C.}$  and that at which the experiment was made.  $D = D' + d \left( .00014 + \frac{1 - D'}{150} \right)$ . When the temperature of the experiment is below  $15.5^{\circ}\text{C.}$ , the fraction  $d \left( .00014 + \frac{1 - D'}{150} \right)$  must be subtracted from  $D'$  instead of being added to it.

"proof spirit" is very confusing, and might with advantage be abandoned. Of this there is little chance at present, as it is adopted in several Acts of Parliament, and is the scale to which Sykes' hydrometer, used by the Excise, has reference. The Excise formerly tested the strength of spirits by pouring a certain amount on gunpowder. A light was then applied. If the spirit was above a certain strength ("proof") the gunpowder ultimately inflamed, but if weaker the gunpowder was too much moistened by the water to be capable of explosion, and the sample was said to be "under proof." By Act of Parliament proof spirit is now defined to be a liquid of such density that at  $51^{\circ}$  F., 13 volumes shall weigh the same as 12 volumes of water at the same temperature. The "proof spirit" thus produced has a density of  $\cdot 91984$  at  $15\cdot 5^{\circ}$  C. ( $=60^{\circ}$  F.), and contains  $49\cdot 24$  per cent. by weight of alcohol and  $50\cdot 76$  of water. Spirits weaker than the above are described by the Excise as being so many degrees or so much per cent. "under proof" (U. P.). Thus, by the term "spirit of 20 per cent. or 20 degrees under proof," is meant a liquid containing, at  $60^{\circ}$  F., 80 measures of proof spirit and 20 of water. "Spirit of  $50^{\circ}$  U. P." contains equal measures of proof spirit and water, while pure water is  $100^{\circ}$  under proof.

On the other hand, spirituous liquids stronger than proof spirit are described according to the number of measures of proof spirit, 100 volumes would yield when suitably diluted with water. Thus, "spirit of  $50^{\circ}$  O. P." is alcohol of such strength that 100 measures at  $60^{\circ}$  F., when diluted with water to 150 measures, would be proof spirit.\* Absolute alcohol accordingly is  $75\frac{1}{4}^{\circ}$  O.P. and contains  $175\frac{1}{4}$  per cent. of proof spirit, for 100 volumes when diluted with water would yield  $175\frac{1}{4}$  volumes of spirit at "proof."

In the following table are given the percentages of abso-

\* Owing to the contraction which occurs on mixing alcohol with water, the volume of water which it would be necessary to add in this instance would be considerably *more* than 50 measures. Thus, a mixture of 100 volumes of rectified spirit with 60 of water only measures 154 volumes instead of 160.

lute alcohol by weight, and of proof spirit by volume, which are contained in mixtures of alcohol and water of various densities:—

## DENSITIES OF VARIOUS MIXTURES OF ALCOHOL WITH WATER.

Specific Gravity at 15·5° C.(=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15·5° C.(=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·79381*	100	175·25	·9090	54·0	108·38
·7969	99	174·19	·9113	53·0	106·64
·8001	98	173·12	·9135	52·0	104·88
·8031	97	171·99	·9160	51·0	103·14
·8061	96	170·86	·9184	50·0	101·39
·8089	95	169·67	·91984†	49·24	100·00
·8118	94	168·48	·9206	49·0	99·60
·8145	93	167·24	·9228	48·0	97·80
·8172	92	165·99	·9249	47·0	95·98
·8199	91	164·73	·9270	46·0	94·15
·8228	90	163·49	·9292	45·0	92·32
·8254	89	162·20	·9314	44·0	90·48
·8279	88	160·86	·9335	43·0	88·62
·8305	87	159·53	·9356	42·0	86·76
·8331	86	158·19	·9376	41·0	84·87
·8357	85	156·83	·9396	40·0	82·98
·8382†	84	155·45	·9416	39·0	81·08
·8408	83	154·08	·9434	38·0	79·15
·8434	82	152·69	·9452	37·0	77·22
·8459	81	151·28	·9470	36·0	75·27
·8483	80	149·84	·9490	35·0	73·34
·8508	79	148·40	·9511	34·0	71·40
·8533	78	146·95	·9528	33·0	69·42
·8557	77	145·47	·9544	32·0	67·43
·8581	76	143·99	·9560	31·0	65·43
·8603	75	142·46	·9578	30·0	63·44
·8625	74	140·92	·9593	29·0	61·42
·8649	73	139·40	·9609	28·0	59·40
·8672	72	137·86	·9623	27·0	57·36
·8696	71	136·32	·9638	26·0	55·33
·8721	70	134·78	·9652	25·00	53·28
·8745	69	133·22	3	24·91	51·22
·8769	68	131·65	4	24·85	49·16
·8793	67	130·07	5	24·77	47·10
·8816	66	128·47	6	24·69	45·04
·8840	65	126·86	7	24·62	43·00
·8863	64	125·24	8	24·54	41·00
·8886	63	123·60	9	24·46	39·00
·8908	62	121·94	·9660	24·38	37·00
·8932	61	120·30	1	24·31	35·00
·8956	60	118·64	2	24·23	33·00
·8979	59	116·96	3	24·15	31·00
·9001	58	115·26	4	24·08	29·00
·9025	57	113·58	5	24·00	27·00
·9047	56	111·86	6	23·91	25·00
·9069	55	110·14	7	23·85	23·00

\* Absolute alcohol.

† Rectified spirit, B.P.

‡ Proof spirit.



Specific Gravity at 155° C.(=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15·5° C.(=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
·9668	23·77	50·73	·9721	19·58	42·03
9	·69	·57	2	·50	41·85
·9670	·62	·41	3	·42	·68
1	·54	·25	4	·33	·51
2	·46	·10	5	·25	·33
3	·38	49·94	6	·17	·16
4	·31	·78	7	·08	40·98
5	·23	·63	8	·00	·81
6	·15	·47	9	18·92	·64
7	·08	·31	·9730	·85	·48
8	·00	·15	1	·77	·32
9	22·91	48·99	2	·69	·16
·9680	·85	·83	3	·62	·00
1	·77	·67	4	·54	39·83
2	·69	·51	5	·46	·67
3	·62	·35	6	·38	·51
4	·54	·19	7	·31	·35
5	·46	·03	8	·23	·19
6	·38	47·87	9	·15	·03
7	·31	·71	·9740	·08	38·87
8	·23	·55	1	·00	·71
9	·15	·39	2	17·91	·53
·9690	·08	·23	3	·83	·36
1	·00	·07	4	·75	·18
2	21·91	46·92	5	·66	·01
3	·85	·76	6	·58	37·83
4	·77	·59	7	·50	·66
5	·69	·43	8	·42	·48
6	·62	·27	9	·33	·31
7	·54	·11	·9750	·25	·13
8	·46	45·95	1	·17	36·96
9	·38	·79	2	·08	·78
·9700	·31	·63	3	·00	·61
1	·23	·47	4	16·91	·43
2	·15	·31	5	·83	·27
3	·08	·15	6	·75	·11
4	·00	44·99	7	·66	35·95
5	20·91	·81	8	·58	·77
6	·83	·63	9	·50	·62
7	·75	·46	·9760	·42	·46
8	·66	·29	1	·33	·30
9	·58	·12	2	·25	·14
·9710	·50	43·94	3	·17	34·97
1	·42	·77	4	·08	·82
2	·33	·60	5	·00	·66
3	·25	·42	6	15·91	·50
4	·17	·25	7	·83	·32
5	·08	·07	8	·75	·14
6	·00	42·90	9	·66	33·96
7	19·91	·73	·9770	·58	·78
8	·83	·55	1	·50	·61
9	·75	·38	2	·42	·43
·9720	·66	·20	3	·33	·26

Specific Gravity at 15.5° C.(=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15.5° C.(=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
.9774	15.25	33.08	.9827	11.08	24.04
5	.17	32.91	8	.00	23.87
6	.08	.73	9	10.91	.67
7	.00	.56	.9830	.81	.47
8	14.91	.38	1	.72	.27
9	.83	.18	2	.63	.07
.9780	.75	31.99	3	.54	22.87
1	.66	.79	4	.44	.67
2	.58	.60	5	.35	.47
3	.50	.41	6	.26	.27
4	.42	.22	7	.16	.07
5	.33	.03	8	.07	21.87
6	.25	30.84	9	9.99	.70
7	.17	.64	.9840	.92	.55
8	.08	.45	1	.85	.40
9	.00	.26	2	.78	.25
.9790	13.92	.10	3	.70	.08
1	.85	29.93	4	.63	20.93
2	.77	.77	5	.56	.78
3	.69	.61	6	.49	.63
4	.62	.44	7	.41	.46
5	.54	.29	8	.34	.31
6	.46	.11	9	.27	.16
7	.39	28.95	.9850	.20	.01
8	.31	.79	1	.12	19.84
9	.23	.62	2	.05	.69
.9800	.15	.46	3	8.98	.54
1	.08	.29	4	.91	.38
2	.00	.13	5	.84	.23
3	12.92	27.97	6	.77	.08
4	.85	.80	7	.70	18.93
5	.77	.64	8	.62	.76
6	.69	.48	9	.55	.61
7	.62	.31	.9860	.48	.46
8	.54	.15	1	.41	.31
9	.46	26.98	2	.34	.16
.9810	.39	.82	3	.27	.01
1	.31	.66	4	.20	17.86
2	.23	.49	5	.13	.71
3	.15	.33	6	.06	.56
4	.08	.16	7	7.99	.41
5	.00	.00	8	.92	.26
6	11.92	25.83	9	.85	.10
7	.85	.66	.9870	.78	16.95
8	.77	.50	1	.71	.80
9	.69	.34	2	.64	.65
.9820	.62	.17	3	.57	.50
1	.54	.01	4	.50	.35
2	.46	24.84	5	.43	.20
3	.39	.68	6	.37	.07
4	.31	.52	7	.30	15.92
5	.23	.36	8	.23	.77
6	.15	.20	9	.16	.62

## DENSITY OF DILUTED ALCOHOL.

Specific Gravity at 15.5° C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15.5° C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
.9880	7.09	15.47	.9933	3.73	8.18
1	.02	.31	4	.67	.05
2	6.95	.16	5	.61	7.92
3	.89	.03	6	.55	.79
4	.82	14.88	7	.49	.66
5	.75	.73	8	.43	.53
6	.69	.60	9	.37	.40
7	.62	.45	.9940	.32	.29
8	.55	.30	1	.26	.16
9	.49	.17	2	.20	.02
.9890	.42	.02	3	.14	6.89
1	.35	13.87	4	.08	.76
2	.29	.74	5	.02	.63
3	.22	.59	6	2.97	.52
4	.15	.43	7	.91	.39
5	.09	.30	8	.85	.26
6	.02	.15	9	.79	.13
7	5.96	.02	.9950	.74	.02
8	.85	12.87	1	.68	5.89
9	.83	.74	2	.62	.76
.9900	.77	.61	3	.57	.65
1	.70	.46	4	.51	.52
2	.64	.33	5	.45	.39
3	.58	.20	6	.39	.25
4	.51	.05	7	.34	.14
5	.45	11.92	8	.28	.01
6	.39	.79	9	.22	4.88
7	.32	.64	.9960	.17	.77
8	.26	.51	1	.11	.64
9	.20	.38	2	.05	.51
.9910	.13	.22	3	1.99	.38
1	.07	.09	4	.94	.27
2	.01	10.96	5	.89	.16
3	4.94	.81	6	.83	.03
4	.88	.68	7	.78	3.92
5	.82	.55	8	.73	.81
6	.76	.42	9	.67	.68
7	.70	.29	.9970	.61	.54
8	.64	.16	1	.56	.43
9	.57	.01	2	.51	.32
.9920	.51	9.88	3	.45	.19
1	.45	.75	4	.40	.08
2	.39	.62	5	.34	2.95
3	.33	.49	6	.29	.84
4	.27	.36	7	.23	.71
5	.20	.20	8	.18	.60
6	.14	.07	9	.12	.47
7	.08	8.94	.9980	.07	.36
8	.02	.81	1	.02	.25
9	3.96	.68	2	0.96	.12
.9930	.90	.55	3	.91	.01
1	.84	.42	4	.85	1.87
2	.78	.29	5	.80	.76

Specific Gravity at 15.5° C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.	Specific Gravity at 15.5° C. (=60° F.)	Percentage of Absolute Alcohol by weight.	Percentage of Proof Spirit by measure.
.9986	0.74	1.63	.9994	0.32	0.71
7	.69	.52	5	.26	.57
8	.64	.41	6	.21	.46
9	.58	.28	7	.16	.35
.9990	.53	.17	8	.11	.24
1	.47	.04	9	.05	.11
2	.42	0.93	1.0000	.00	.00
3	.37	.82			

In the part of the table referring to spirit containing more than 25 per cent. of real alcohol, only those densities are given which correspond to exact units by weight of alcohol, but the part of the table referring to spirit containing less than 25 per cent. of absolute alcohol is more extended, every density to four places of decimals having the corresponding percentage of absolute alcohol and proof spirit stated. Hence, when it is desired to take the density of strong spirit, the sample may be diluted with exactly its own weight (not measure), or twice its weight of water, so as to bring the density to a more accurate part of the table, the percentage of absolute alcohol found being subsequently multiplied by two or by three according to the extent to which the sample was previously diluted. In such cases the percentage of proof spirit should be ascertained from the percentage of alcohol calculated upon the original sample, and not by doubling or tripling the amount corresponding to the density of the diluted spirit.

Another plan is to ascertain the exact percentage of alcohol by the system of interpolation. The following example shows its application to a sample of spirit of .9550 specific gravity:—

$$\frac{.9560 - .9550}{.9560 - .9544} = \frac{.0010}{.0016} = \frac{5}{8} = .625, \text{ and}$$

$$.625 + 31.0\% = 31.625\% \text{ of real alcohol in spirit of .9550 sp. gr.}$$

The percentage of alcohol by weight, multiplied by the density of the spirit, and this by 2.208, gives the percentage by volume of proof spirit contained in the sample.



In France, Belgium, Germany, Sweden, the United States, &c., spirits are valued by the percentage *volume* of alcohol contained in them. This may be ascertained from the preceding table by multiplying the percentage of proof spirit by the factor  $\cdot 5706$ . Similarly, by multiplying the percentage of alcohol by weight by the observed specific gravity, and dividing the product by  $\cdot 7938$ , the percentage of alcohol by volume is obtained. Thus, proof spirit has a density of  $\cdot 91984$ , and contains  $49\cdot 24$  per cent. of alcohol by weight. Therefore, it contains

$$\frac{\cdot 91984 \times 49\cdot 24}{\cdot 7938} = 57\cdot 06 \text{ of alcohol by volume.}$$

By multiplying the percentage of alcohol by volume contained in a liquid by the factor  $1\cdot 7525$  (or dividing by  $\cdot 5706$ ) the percentage volume of proof spirit is obtained.

When it is required to calculate what proportion of proof or any other strength of spirit a particular sample of alcohol contains, or would contain when diluted, the following formula should be used:—

$$\frac{\text{Percentage of proof spirit in alcohol required} \times 100}{\text{Percentage of proof spirit in sample}} = \left\{ \begin{array}{l} \text{The number of volumes of the stronger} \\ \text{spirit which will produce or be con-} \\ \text{tained in 100 measures of the more} \\ \text{dilute spirit,} \end{array} \right.$$

Thus, if it be required to know what percentage of gin at  $20^\circ$  U. P. is contained in a watered sample of  $44^\circ$  U. P., the following calculation will suffice:—

$$\frac{56 \times 100}{80} = 70 \text{ per cent. by volume. Hence the sample is}$$

of a strength corresponding to the dilution of 7 gallons of gin at  $20^\circ$  U. P. to 10 gallons by addition of water.

Again, to ascertain the proportion of water which must be added to spirit at  $35^\circ$  O. P., to reduce the strength to  $10^\circ$  U. P.

$$\frac{90 \times 100}{135} = 66\cdot 7. \text{ That is to obtain spirit of } 10^\circ \text{ U.P. } 66\cdot 7$$

measures of spirit at  $35^\circ$  O. P. must be diluted to 100, or every two gallons must be made up to three by addition of water.

2. For very small quantities of alcohol, Dupré's method is very useful (see page 93).

3. Duclaux\* has described a method of determining alcohol based on the surface tension of the liquid, or, in other words, on the number of drops of the spirituous liquid which are delivered by a pipette constructed to deliver 100 drops of water. The pipette is conveniently of about 5 c.c. capacity, and the experiment must be conducted at a temperature of 15° C. The following table shows the number of drops given by pure alcohol of various dilutions and of wine of various alcoholic strengths :—

Alcohol (by volume).	No. of Drops at 15° C.		Alcohol (by volume).	No. of Drops at 15° C.	
	Spirit.	Wine.		Spirit.	Wine.
0 per cent.	100	—	15 per cent.	160	169
1 "	107	—	16 "	163½	—
2 "	113	—	17 "	167	—
3 "	118	119½	18 "	170	—
4 "	122½	124	19 "	173	—
5 "	126½	128½	20 "	176	—
6 "	130½	132½	25 "	192	—
7 "	134	137	30 "	204½	—
8 "	137½	141	40 "	225½	—
9 "	140½	145½	50 "	243	—
10 "	144	149½	60 "	351	—
11 "	147	153½	70 "	255½	—
12 "	150½	157½	80 "	258½	—
13 "	154	161½	90 "	261½	—
14 "	157	165½	100 "	270	—

It is evident that this method is chiefly of service for very dilute alcohol, but under favourable circumstances, M. Duclaux claims that the method gives, in a few minutes, results of greater accuracy than can be obtained by a hydrometer. The presence of very minute proportions of acetic ether or butyric acid increases the number of drops very sensibly.

4. Another method of determining alcohol, which is sometimes very useful, is based on the tension of its vapour, which is greater, under the same circumstances, the richer the liquid is in spirit. The determination is best effected by an apparatus

\* *Ann. Chim. et Phys.* [5] ii. 233.

sold as "Geissler's Vaporimeter," with which full working details are given.

5. A colorimetric method of determining alcohol has been described by M. Monell.\* It is based on the fact that the addition of nitrate of cobalt to an alcoholic solution of ammonium thiocyanate (sulphocyanide) produces a deep blue colour which disappears on dilution with water, and is restored by a further addition of alcohol. If a measured quantity of this deep-blue liquid be poured into a cylinder and the liquid to be tested be added till a certain standard tint is reached, the volume of the mixed liquids will be greater the more alcohol the sample contains. The standard tint may be obtained by the use of a sample containing a known proportion of alcohol, and if it be made the same as a piece of cobalt-blue glass the latter may be substituted for it in subsequent experiments. The blue solution of cobalt thiocyanate must always be prepared with alcohol of the same strength.

Other plans for the determination of alcohol have been based on its rate of dilatation by heat, and on its boiling point. These methods are capable of being used with advantage under special circumstances, but they require special apparatus and are generally less accurate and convenient than those already given. For the general purposes of the laboratory the determination of alcohol by its density is by far the best plan.

FOR THE DETERMINATION OF VERY SMALL QUANTITIES OF ALCOHOL† the following method described by A. Dupré‡ may be very advantageously used. It was first proposed by E. Chapman, and is based on the fact that when alcohol is heated with chromic acid it is oxidised to acetic acid, which may be distilled off and titrated with accuracy by standard alkali.

In practice, a weighed amount of spirituous liquid is taken

\* *Journ. Chem. Soc.* 1878, ii. 246.

† For Thresh's approximate method of determining small quantities of alcohol see page 81.

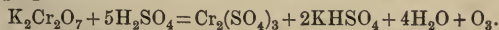
‡ *Journ. Chem. Soc.* xx. 495.

which will contain about 0.1 gramme (not more than 0.2) of real alcohol.\* This is made up to about 20 c.c. by addition of water, and is placed in a small strong flask. A liquid is next prepared containing in each 100 c.c., 10 grammes of potassium bichromate and 20 grammes (or 11.8 c.c.) of strong sulphuric acid, the volume being made up with water.† 10 c.c. of this chromic acid solution are introduced into the flask, which is then securely closed by an india-rubber stopper tied down, and suspended in a bath of boiling water for two hours, by which time all the alcohol will have been oxidised to acetic acid. After cooling, the flask is opened and sulphuric acid and granulated zinc added to reduce the excess of chromic acid. The green liquid is then distilled, pumice or tobacco-pipe being added to prevent bumping. When nearly dry, water should be added and the distillation repeated. The acetic acid in the distillate is then determined by titration with decinormal caustic soda, as described on page 189. Before commencing the titration it is desirable to add a drop or two of barium chloride as a test for sulphuric acid. Any precipitate must be filtered off, and 46 parts of alcohol subtracted for every 233 of barium sulphate obtained. Each c.c. of decinormal alkali required represents 0.0046 of real alcohol in the liquid examined. In presence of acetic acid or foreign fixed matter, the spirituous liquid must be rendered slightly alkaline and distilled,‡ the chromic acid solution being applied to the distillate or a portion of it.

THE DETERMINATION OF ALCOHOL IN PRESENCE OF FIXED MATTERS cannot be effected directly by the specific gravity method, but approximate results can be obtained by several of the alternative processes already given. The indirect deter-

\* Larger quantities may be used if the proportions of water and oxidising mixture are duly increased.

† These proportions are sufficient for the reaction—



‡ A further concentration of the alcohol by redistillation from a slightly acid liquid is often desirable.



mination by the density may be effected in wine and beer with moderate accuracy in the following manner:—

1. The specific gravity of the original liquid is first accurately observed. A measured quantity, such as 100 c.c., is then boiled sufficiently long to volatilise all the alcohol, and the “extract” subsequently made up with water again to the exact original bulk, the dilution being executed at 15.5° C. (=60° F.). Then,

$$\frac{\text{Specific gravity of original liquid}}{\text{Specific gravity of the “extract”}} = \text{Specific gravity of the alcohol evaporated.}$$

From the last figure the proportion of alcohol can be ascertained by reference to the table, page 85, *et seq.*

2. The following method for the determination of alcohol in wines and other alcoholic liquids containing fixed matters is of very general application and is thoroughly satisfactory.

50 c.c. of the sample are accurately measured at 15.5° C. (=60° F.). In the case of beer and other liquids weak in spirit, 100 c.c. may be appropriately taken. Any free acid in the sample is next neutralised by a cautious addition of caustic soda, which should be used in amount sufficient to impart a slight alkaline reaction. About .1 gramme of tannin is next added (to prevent frothing), and the liquid is made up with water to about 150 c.c.

It is next placed in a small retort or flask fitted air-tight to a Liebig’s condenser, or similar arrangement allowing of thorough cooling of the vapours, and is distilled by a gentle heat, the distillate being collected in a flask holding 100 c.c. When the distillate has a volume within a few centimetres of this quantity, the operation is arrested, the distillate thoroughly mixed by agitation, and brought to a temperature of 60° F. when it is made up to exactly 100 c.c. by addition of distilled water at 60° F. The liquid is again well mixed, and the density carefully taken by a 50 c.c. specific gravity bottle, or a Sprengel’s tube, when a reference to the table (page 85) will at once show the percentage of alcohol by weight contained in the distillate. Then,

Density of distillate  $\times$  measure of distillate in c.c.  $\times$  per cent. of alcohol found in distillate by table

Density of sample  $\times$  measure of sample taken in c.c.

= Percentage of absolute alcohol by weight contained in *the sample*.

This calculation involves the necessity of knowing the *density* of the *original sample*. If unknown, the determination may be avoided by carefully weighing the 50 or 100 c.c. taken for the experiment, and substituting this weight in grammes for the denominator of the above fraction.

The calculation can be wholly avoided, and a more satisfactory result obtained by *weighing* the original sample instead of measuring it, and also weighing the distillate. About 50 grammes of the sample should be taken, and the distillate may conveniently be made up to about 100 c.c. and weighed. After thoroughly mixing the liquid its density is taken, when,

Weight of distillate  $\times$  percentage of alcohol found in distillate by table

Weight of sample taken.

= Percentage of absolute alcohol by weight contained in *the sample*.

In the case of strong spirituous liquids, the sample may be advantageously diluted to four times (instead of three times) its original bulk before commencing the distillation, the boiling being continued till three-fourths (instead of two-thirds) of the entire liquid has passed over.

To avoid loss of alcohol by imperfect condensation, it is desirable, when small quantities are to be determined, or very accurate results are required, to use an apparatus in which the retort and receiver are both connected air-tight with the condenser. A suitable receiver for the purpose is a small cylinder graduated at 50, 100, and 150 c.c., and furnished with an indiarubber stopper pierced with two holes, through one of which passes the end of the condenser tube, while the other carries a safety-tube, or funnel, closed by mercury. By operating in this manner, a certain contraction and expansion of the contained air is permitted, while all loss is prevented. When the amount of the distillate approaches the desired volume, the receiver is detached, and the contained

liquid transferred to a flask or suitable vessel for weighing or measuring, the volume being made up with the rinsings of the receiver.

In the case of very weak alcoholic liquids, a second distillation from a faintly acid liquid is often desirable.

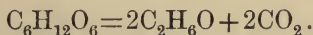
Distillation from a neutralised liquid suffices to separate alcohol from fixed substances like sugar and salt, from acids (*e.g.*, acetic), and from bodies of high boiling point, such as glycerin. In presence of ether, chloroform, and other readily volatile bodies, the distillate will contain them, and must be subsequently examined by special methods adapted for the particular case in question. Methods for the examination of mixtures of alcohol with ether, chloroform, amyl alcohol, &c., will be found in the sections treating of these bodies. From compound ethers generally, alcohol is best separated by treating the distillate with twice its measure of a saturated aqueous solution of calcium chloride, in which most of the ethers are insoluble. In other cases the separation may be effected by adding anhydrous calcium chloride, with which any water and alcohol combine, while the ethers may be distilled off by the heat of a water-bath. By subsequently adding water, the alcoholic compound with chloride of calcium is decomposed, and the alcohol may be obtained by distillation. Fractional distillation may be conveniently employed in some cases. Any determination of the alcohol in such mixtures will generally be merely approximate, though in special cases fairly good results are obtainable. (See articles on ether, compound ethers, chloroform, methyl alcohol, amyl alcohol, tinctures, &c.)

**Production of Alcohol; Fermentation.**—In the laboratory, the synthesis of ethyl alcohol has been effected by several methods, but in practice it is always produced by the fermentation of saccharine matter. This exists ready formed in the grape, but when alcohol is produced from grain the starch of the seed is first converted into sugar, and this subsequently changed to alcohol.



Although various kinds of sugar can be used for the production of alcohol, glucose appears to be the only kind capable of direct alcoholic fermentation, other kinds of sugar undergoing a previous conversion into glucose.

The change of the starch of grain, malt, or potatoes into glucose is effected by a peculiar nitrogenised ferment called diastase, the proportion of which in malt does not exceed  $\cdot 002$  or  $\cdot 003$  per cent. of its weight. Subsequently, under the action of the yeast-ferment (*Torula cerevisiæ*), the glucose becomes split up into alcohol and carbonic acid, thus:—



In the case of the fermentation of grape-juice the change is brought about by a ferment existing on the skins of the fruit. In all cases the production of alcohol is accompanied by evolution of gas and “attenuation” or decrease in the specific gravity of the liquid. According to the nature of the liquid and the management of the process, the product is wine, beer, cider, koumiss, &c. By distillation, the alcohol can be separated from the fixed matters, and is then known as cognac, whisky, rum, &c., according to its origin.

Ethyl alcohol and carbonic acid are the chief, but by no means the only products of vinous fermentation. The higher homologues of ethylic alcohol are almost always produced in small, and sometimes in considerable amount. By exposure to the air, acetic acid and its homologues are produced, and these react on the alcohols with production of various compound ethers. Glycerin and succinic acid also appear to be constant products of alcoholic fermentation. 100 grammes of sugar, when fermented with yeast, yielded Pasteur  $\cdot 673$  grammes of succinic acid, and  $3\cdot 640$  grammes of glycerin. Under certain conditions lactic acid, butyric acid, and other bodies are formed.

**Wine.**—Wine is, strictly speaking, the fermented juice of the grape. Chemically, wine is a liquid containing from 6 to



13 per cent. by weight of absolute alcohol, more or less unconverted sugar, tannin, colouring-matter, and salts. The acidity of genuine wine is due chiefly to the acid tartrate of potassium, though free acetic and other acids are also present, especially if the wine has been exposed to the air. The bouquet of wine is due to small quantities of certain ethers, notably ethyl acetate and pelargonate. These may be detected and determined by the process given on page 142. The alcohol of wine can be accurately determined by the distillation process described on pages 94 and 95. The volatile acids of wine may be examined as on page 215; the acetic acid can be estimated as described on page 192, and the tartaric acid and tartrates as on page 249, *et seq.* The determination of succinic acid, glycerin, and tannin in wine is also described under those respective heads. The chemistry and complete analytical examination of wines are very complicated, and would require more space than can be devoted to them in this volume.\*

**Beer, Ale,** and other **Malt Liquors** are produced by the fermentation of barley or other saccharine matter, hops, &c. being used for flavouring purposes. Chemically, beer is a liquid containing from 2 to 8 per cent. by weight of absolute alcohol, together with more or less unconverted sugar, dextrin, salts, &c. The acidity of beer is usually ascribed to acetic acid, but, except in sour ales, is more probably attributable to lactic acid. A ferment producing lactic acid is present to a greater or less extent in most yeast.† The determination of the alcohol in malt liquors may be readily effected by the dis-

\* The most complete treatise on the chemistry of wine is that of Thudichum and Dupré (*A Treatise on the Origin, Nature, and Varieties of Wine*, London, 1872). Much information also is contained in Hassall's *Food and its Adulterations*, 1876; Blythe's *Practical Chemistry*, 1878; and A. B. Prescott's *Chemical Examination of Alcoholic Liquors*, 1875.

† The relationship existing between glucose, lactic acid, and acetic acid is well shown by a comparison of their formulæ, one molecule of glucose,  $C_6H_{12}O_6$ , having the composition of two molecules of lactic acid,  $C_3H_6O_3$ , or three of acetic acid,  $C_2H_4O_2$ .

tillation process (pages 94 and 95). The free acid may be determined as in vinegar. The total extractive matter may be determined by evaporating 10 c.c. of the sample to dryness, and drying the residue at 100° C. After weighing, the residue may be ignited, and thus the proportion of mineral matter learned.

Further details of the chemistry and mode of examination of beer are deferred. (See also articles on succinic acid, picric acid, salicylic acid, and glycerin).

**Cider and Perry.**—These are alcoholic drinks obtained by the fermentation of apple and pear juices respectively. In their general characters they resemble beer, but are peculiar in containing malic acid.

The following is the average composition of cider as deduced by M. Rousseau from the analysis of twenty samples of the Brittany produce:—

Alcohol (by volume)	. . .	2.05 per cent.
Residue on evaporation	. . .	1.93 „
(containing sugar	. . .	.25 „ )
(yielding ash	. . .	.152 „ )

The results of M. Rabot are widely different. According to this observer, good ordinary cider, after a year's keeping, should contain 5 to 6 per cent. of alcohol, and 30 grammes per litre of extract, yielding 2.8 grammes of ash, of which 2.15 consist of salts soluble in water.

Perry is richer in alcohol than cider, as might have been expected from its greater content of sugar. The proportion of sugar contained in samples of cider made from six varieties of apple has been determined by M. Truelle. From the fact that a portion of the sugar exerts no reducing action on Fehling's solution, cider appears to contain cane—or more probably some peculiar variety of—sugar. In the following table are given M. Truelle's determinations of sugar, together with the acidity of the ciders expressed in terms of free malic acid:—

1. 1.1111 2. 1.1111 3. 1.1111 4. 1.1111 5. 1.1111 6. 1.1111

	Sugar, per Cent.			Acidity.
	Reducing.	Non-reducing.	Total.	
No. 1.	9·64	·83	10·47	·189 per cent.
No. 2.	8·03	1·71	9·74	·149 „
No. 3.	9·53	1·21	10·74	·263 „
No. 4.	7·79	1·76	9·55	·189 „
No. 5.	8·62	1·80	10·42	·149 „
No. 6.	9·64	·46	10·10	·527 „

Cider is liable to several diseases, such as a formation of acetic acid through secondary fermentation. Another curious affection is the “killing” or blackening, due to the conversion of the malates into carbonates under the influence of a ferment. Cider so affected becomes of a violet-black colour, a symptom which may be remedied by addition of tartaric acid.

Cider is liable to be sophisticated by addition of water, colouring-matters, &c.; by the use of lime, chalk, soda, &c., as anti-acids; and by the addition of litharge, white-lead, or sugar-of-lead as clarifying agents. Zinc and copper have also been met with.

POISONOUS METALS in cider may be searched for in the following manner:—100 c.c. of the sample are evaporated to dryness, and the residue gently ignited in porcelain. The ash is moistened with nitric acid and again ignited, the treatment with nitric acid being repeated till all carbon is consumed.

The residue is next treated with a few drops of strong sulphuric acid, and heat applied till the acid begins to volatilise. Water is then added, and the liquid filtered. Any lead remains as  $\text{PbSO}_4$ , which may be washed slightly, and recognised as lead sulphate by its solubility in a hot alkaline solution of ammonium acetate, the liquid produced giving a chrome-yellow precipitate on being acidified with acetic acid

and treated with chromate of potassium. From the weight of chromate of lead obtained (dried at  $100^{\circ}\text{C}.$ ) the amount of lead present can be calculated.  $\text{PbCrO}_4 : \text{Pb} :: 323 : 207$ . In the sulphuric acid solution of the ash, copper may be directly detected by adding potassium ferrocyanide; but the brown colour, indicative of copper, is liable to be obscured by the blue precipitate produced in presence of iron. It is therefore preferable to neutralise the excess of acid with ammonia, boil with ammonium acetate, filter off the ferruginous precipitate, and test the filtrate for copper. A brown precipitate, or reddish-brown coloration, will be produced on adding potassium ferrocyanide, if copper be present. Zinc gives a white precipitate. If sulphuretted hydrogen be employed instead, the copper is precipitated as black cupric sulphide and the zinc as white zinc sulphide. If the presence of both metals be suspected, they may be separated by filtering off the precipitate produced by sulphuretted hydrogen, dissolving it in bromine water, boiling off the excess of bromine, and precipitating the copper by sulphuretted hydrogen, a galvanic current, a thiocyanate and alkaline sulphite (page 60), or other convenient method. When either of these methods is employed, the zinc remains in solution. They may be applied equally well to the sulphuric acid solution of the ash, as far as copper is concerned. Zinc may also be detected by the method described under vinegar (p. 201).

Another method of examining the ash is to precipitate the sulphuric acid solution with a large excess of ammonia, and filter off the iron and phosphates. In presence of any considerable amount of copper the filtrate is blue. Traces of copper may be detected by boiling off the larger part of the ammonia, acidulating the liquid with acetic acid, and adding potassium ferrocyanide, when a brown colour will be developed. If zinc only be present, the precipitate will be white. Zinc may also be detected by adding potassium ferro-



cyanide to the boiling ammoniacal solution, when a white precipitate will be thrown down even if only a trace of zinc be present. Small quantities of copper do not interfere.

A good general method for the examination of an ash for poisonous metals is to separate the lead, as above described, precipitate the copper on the inside of a platinum crucible by the current from one cell of Grove's battery, to nearly neutralise the residual liquid with ammonia, and boil it with bromine water and ammonium acetate, and precipitate the zinc from the filtrate by passing sulphuretted hydrogen. Any tin remains insoluble on treating the sulphate of lead with ammonium acetate.

The presence of free mineral acids in cider may be detected as described under vinegar (p. 198).

**FICTITIOUS CIDER** is sometimes prepared by fermenting starch sugar, and adding vinegar, cinnamon, &c. An effervescent preparation, said to be manufactured from turnips, is much sold in Manchester and the neighbourhood, under the name of "champagne cider."

**Spirits.**—Under this term are comprehended the various liquids obtained from alcohol-containing liquors by distillation. Wheat, oats, rye, barley, Indian corn, rice, and other grains, whether in the raw or the malted state, as well as the juices of fruits, sugar-cane, beetroot, potatoes, carrots, and even some of the grasses, may be made to yield alcohol by fermentation. When the resulting alcoholic liquid is distilled, a "spirit" is obtained, which is known under various names, according to circumstances. Thus, British spirits (whether brandy, gin, whisky, or rum), are produced from corn; "cognac," or French brandy, from wine; West Indian rum, from sugar or molasses. The different qualities of these various liquids depend partly on the percentage of alcohol contained in them, partly on the mode of manufacture pursued, partly on the berries, seeds, herbs, &c., with which they are flavoured, and, lastly, on the substances from whence the spirits are derived.

The object of the distillation is, of course, in every case to separate the alcohol from the non-volatile matters, such as husk, fibre, inorganic salts, undecomposed yeast, lactic and succinic acids, glycerin, &c. The volatile products are, besides water, chiefly ethylic alcohol, fusel oil (see page 120), and acetic acid. The presence of fusel oil is very objectionable (see page 116), and one of the chief objects of the distiller should be so to manage the process as to effect its separation from the spirit as completely as possible. This can be partially effected by careful distillation alone; but soap, milk, charcoal, and other "physics" are also of more or less service.

After the first operation, or "distillation," which produces a crude alcohol, the product is redistilled or "rectified." The prosecution of this process constitutes a distinct business from that of the distiller proper.

ARRACK is a name which is properly applied to a spirit distilled from toddy, the juice of the cocoa-nut tree. Batavian and Jamaica arrack are, however, manufactured from molasses and rice, with a little toddy.

BRANDY, strictly speaking, is a spirit obtained by the distillation of wine. The "marc" of grapes and other refuse products obtained in the manufacture of wine are frequently employed for the production of an inferior quality of brandy. Such a product contains much more fusel oil than is present in the superior variety. The peculiar flavour and aroma of "cognac," or French brandy, are due to the presence of ethyl pelargonate ("cenanthic ether"), and other secondary products of fermentation. When freshly distilled, brandy is perfectly colourless, but it readily takes up colouring-matter from the storing casks, and caramel and similar colouring agents are frequently added to it. It often contains traces of tannin and free acid. Artificial or British brandy is manufactured by flavouring grain spirit. Among the flavouring agents employed for the purpose are acetate, nitrite, and pelargonate of ethyl; oils of cassia, cloves, and bitter-almonds;

tinctures of allspice, galls, capsicum, oak-bark, &c.; burnt sugar, and other colouring materials. Another very perfect imitation-cognac is prepared by distilling proof spirit with argol, bruised prunes, and a little real cognac. The distillate is then coloured with caramel and flavoured with tannin.

GIN is a colourless neutral spirit, originally obtained from grain. The grain spirit is treated with oil of juniper, turpentine, or other flavouring agents, and again distilled. Gin is usually very free from fusel oil, free acid, tannin, &c. It is not unfrequently adulterated. Sugar is a normal constituent of sweetened gin. Salts of zinc and lead have occasionally been met with in gin, and alkaline solutions, such as carbonate of potassium, are sometimes added. Among the substances used for flavouring gin are juniper berries, oil of juniper, turpentine, almond-cake, coriander seeds, cardamom seeds, grains of paradise, capsicums, calamus, orris and angelica roots, &c. Gin is frequently largely diluted with water.

HOLLANDS and SCHNAPPS are varieties of gin.

KIRSCHWASSER, or KIRSCH, is a spirit obtained by the distillation of the fermented juice of the wild cherry. It is prepared chiefly in the Black Forest, Switzerland, and certain departments of France.

Kirschwasser usually contains about 90 per cent. of proof spirit. It contains, as a normal constituent, a small proportion of prussic acid. In good specimens this usually amounts to not more than one grain to the pint, but inferior specimens often contain three or four times this amount. Kirschwasser also frequently contains distinct traces of copper; so constantly is this metal present, that it has been regarded as indicating the genuine nature of the spirit. It is evident that this presumption is very fallacious, as the presence of copper entirely depends on the use of an apparatus of that metal for distillation, and copper could readily be added to a spurious article. Kirschwasser is often mixed



with alcohol from other sources, or is made entirely from grain spirit, flavoured with peach blossoms or cherry-laurel leaves. The excessive proportion of hydrocyanic acid in such preparations indicates their origin. The addition of cherry-laurel water is indicated by the same means. According to Boudet, such kirschwasser contains .220 grammes of HCy per litre. A preparation is sometimes sold as kirschwasser, consisting of dilute alcohol, somewhat sweetened and flavoured with oil of bitter-almonds, and occasionally nitrobenzene has been substituted for the last ingredient. These additions may be detected by distilling off the alcohol at a low temperature, shaking the residual liquid with ether, and examining it for benzoic aldehyde and nitrobenzene. The proportion of hydrocyanic acid in kirschwasser may be determined as described on page 32, and any copper may be detected and estimated by evaporating the spirit to dryness, igniting the residue, dissolving in dilute nitric acid, and employing the usual methods (see page 100).

RUM.—This spirit was formerly wholly obtained by distillation of the alcoholic liquid obtained by fermenting the juice of the sugar-cane. It is now made largely from molasses and other residual products of the manufacture of sugar from the sugar-cane, beetroot, &c. The characteristic flavour of rum is due to the presence of ethyl butyrate (butyric ether). A fictitious rum is largely prepared by flavouring grain spirit with butyric ether, or even by adding butyric acid, which gradually forms ethyl butyrate by reacting with the alcohol present. Occasionally, sliced pine-apples are used for flavouring. Brown rum always contains caramel or similar colouring matters.

WHISKY is a variety of spirit distilled from fermented grain or potatoes. In some cases, the barley, or other grain, is first malted, but in others it is used raw. In the majority of cases a judicious admixture of raw and malted grain is employed. Other things being equal, the spirit from malted grain is the



most valuable, and contains least fusel oil. Whisky improves greatly on keeping, owing to the conversion of the fusel oil into other bodies.

Whisky usually contains a trace of volatile acid, the proportion of which rarely or never reaches '1 per cent. (in terms of acetic acid). When new it is colourless, or nearly so; but by storing in sherry casks—a favourite mode of imparting flavour to whisky—it acquires colour, and then contains sensible traces of tannin, sugar, &c. The residue left on evaporating whisky to dryness on the water-bath should not exceed 100 grains per gallon, and is usually much less. The smoky flavour of whisky is due to empyreumatic products formed in the distillation, but is often imitated by adding one or two drops of creasote to the gallon of spirits. Logwood, catechu, tea infusion, burnt sugar, &c., are sometimes added as colouring agents. Wood naphtha has been occasionally used as an adulterant of whisky. It is very doubtful whether fusel oil is ever purposely added to whisky, but it is almost invariably present in greater or less quantity, and is the cause of the objectionable symptoms produced by new spirit (see pages 116 and 120). Alkaline solutions (*e.g.*, carbonate of sodium), salts of zinc, lead, and copper, and other objectionable matters, have been occasionally added to whisky.

THE CHEMICAL EXAMINATION OF SPIRITS is sometimes very difficult, and in the present state of our knowledge the recognition of the flavouring agents is often impossible. The following are the chief points to which attention should be directed:—

DETERMINATION OF THE ALCOHOL. This may be effected with accuracy by the methods described on page 82, *et seq.*

THE DETECTION OF METHYL ALCOHOL may be effected as described on page 71, *et seq.*

FUSEL OIL may be detected and approximately estimated as described on page 120, *et seq.*

THE NON-VOLATILE RESIDUE is sometimes of importance. When freshly distilled, spirits contain no trace of non-volatile matter. When kept in casks they take up more or less fixed matter, but the amount rarely exceeds 100 grains per gallon. It consists of tannin, tartrates, sulphates, traces of sugar, &c. The proportion of non-volatile matter in spirits is ascertained by evaporating 50 or 100 c.c. to dryness on a water-bath. Some indication of its nature may be obtained by tasting the residue. On ignition in the air, any zinc, lead, or copper present in the spirit will be left as an oxide. Very sensible traces of these metals may be present accidentally, and there is good evidence that their salts have been occasionally used as adulterants. Occasionally, clarifying materials are employed of which lead acetate forms a constituent. Alum is also used occasionally. The reaction of the ignited residue should be observed, as, if alkaline, an alkaline carbonate, acetate, tartrate, &c., must have been present.

SULPHATES will be detected on adding barium chloride to the diluted spirit. Free sulphuric acid has been met with in whisky, and is said to have been formerly freely used for adulterating gin. This is extremely improbable. The presence of free sulphuric acid may be detected by the methods used for examining vinegar for mineral acids (see page 198).

FREE ACID may exist in brandy, &c., as a natural constituent of the distilled liquid. The amount due to this cause is very small, and the acid so present is wholly volatile. The proportion of total free acid may be ascertained by titrating the spirit with standard alkali, and if the volatile acid be distilled off from another portion of the sample, the relative proportions of fixed and volatile acid may be ascertained, and calculated to tartaric and acetic acids respectively.

TANNIN is often present in brandy, &c., being chiefly extracted from the casks used for storing. Sometimes it is purposely added in the form of tincture of galls or oak-bark.

It may be detected by the darkening produced on adding ferric chloride to the spirit.

CARAMEL (burnt sugar) is used for colouring and flavouring spirits, and is left as a brown residue on evaporating the spirit on the water-bath. It is distinguished by its bitter taste, its power of reducing Fehling's solution, &c.

SUGAR, when present, must always have been added subsequently to the distillation. Its presence is legitimate in the case of gin, which is more strictly a *liqueur* than a simple spirit. Gin being perfectly neutral in reaction, the cane-sugar added undergoes no change; but in acid spirits it is usually converted into glucose.

HEAVY METALS, such as lead and copper, may be detected in the original spirit by sulphuretted hydrogen, with the addition, when zinc is to be sought for, of sodium acetate. They may also be detected and estimated in the matter left on evaporating the sample to dryness and igniting the residue.

THE FLAVOURING AGENTS added to spirits are usually employed in such small quantity that any attempt to identify them is almost hopeless, except under very favourable circumstances. The varied nature of the flavours used is indicated in the description of the special characters of the different kinds of spirits. The various ethers employed are, as a rule, more volatile than the remainder of the spirit, and hence become concentrated in the first portions which distil over. In these, they may sometimes be recognised by their odours, and occasionally, but rarely, by their chemical characters. The active principles of a few flavouring agents are fixed, and thus remain in the residue when the spirit is evaporated. This is the case with *capsicum* (cayenne). In spirits flavoured with this material the residue left on evaporation has a hot pungent taste. A still more characteristic property is observed on heating the residue. If *capsicum* be present, on smelling the fumes an intolerably pungent odour will be

noticed, and a burning sensation produced in the lungs. The same effects are obtainable by smelling the fumes arising from heated cayenne pepper. The author has observed the production of the irritant fumes in cases in which the residue was free from marked pungent taste, but he was unable to identify the substance present. Convictions have occurred for selling gin adulterated with cayenne. Nitrobenzene has been added to spirits; but the quantity used must be very small. It may be detected by distilling off the alcohol, agitating the residue with ether, removing the ethereal layer with a pipette, allowing the solvent to evaporate, and treating the residue with zinc and hydrochloric acid, as described under "benzoic aldehyde."

THE ALCOHOLIC STRENGTH OF SPIRITS is unfortunately not definitely fixed at present by any legal standard (see note, page 110). It is extremely difficult to say at what point of dilution any particular spirit, such as gin, ceases to be gin, and becomes gin and water. Nevertheless, there have been numerous convictions of late years for selling gin adulterated with water, and hence the following considerations are of interest:—

All spirits consist of more or less diluted alcohol, containing small proportions of flavouring agents. When spirits are stored in casks they lose strength with a rapidity depending on their percentage of alcohol, the mode of storage, &c. In an atmosphere saturated with aqueous vapour, the alcohol alone evaporates very rapidly, but in a dry atmosphere water also will volatilise, and hence the spirit will not lose so greatly in strength. By keeping, the fusel oil becomes more or less changed and converted into certain ethers, the presence of which materially enhances the value of the spirit. Hence the alcoholic strength of spirits is not the only factor to be considered in judging of their money value or wholesomeness, although the other considerations are far less tangible.

In the trade, the gin sent out to the retailers is chiefly of two strengths, 17° and 22° under proof (see page 84). (Messrs



Gilbey and a few other firms also supply a still weaker gin at a correspondingly low price). As a few degrees in addition may readily be lost by evaporation during the process of racking, or by simply keeping the spirit, it would be unfair to assert that the gin had been watered unless weaker than 27° or 28° under proof. Practically, then, the limit at which gin becomes so dilute as to be adulterated with water may be taken at 34 per cent. by weight of absolute alcohol, equal to 28·6° under proof. This is a strength quite low enough to permit of every allowance for natural deterioration. If the retailer bought the spirit at a still lower strength, the onus of the proof of the fact should lie with him.

In the appeal case of *Pashler v. Stevenilt*, heard before Baron Cleasby and Mr Justice Grove, it was held by the court that gin ought not to be weaker than 20° under proof. As many convictions have taken place on the strength of this decision, it is well to calculate the proportion of water added by the retailer on the assumption that the spirit sold him was of this strength. The method of calculation is described on page 90.

In the case of rum, brandy, and whisky, there have hitherto been no authoritative decisions as to alcoholic strength; but it is generally admitted that they should be stronger than gin.\*

**Liqueurs or Cordials.**—Under these names are included a number of special and proprietary drinks consisting of grain spirit heavily sweetened and flavoured. They are sometimes brightly coloured; indigo, cochineal, turmeric, and gamboge are among the least objectionable agents employed, while aniline dyes, picric acid, and salts of copper are occasionally used. Sweetened gin is, strictly speaking, a *cordial*

\* The "Sale of Food and Drugs Amendment Bill" contains a clause defining the strength of spirits. On the recommendation of the Select Committee (based on the evidence given by Mr Bell of the Inland Revenue Laboratory, April 22, 1879), the minimum limit of strength for gin will probably be fixed by law at 35° U.P., and that for brandy, rum, and whisky at 25° U.P.

rather than a true *spirit*. Among the most popular liqueurs may be mentioned absinthe, curaçoa, maraschino, and noyeau.

Robur, or tea-spirit, which had a short-lived popularity due to extensive advertising, consisted of grain spirit, strongly sweetened and mixed with infusion of tea-leaves. Cherry-brandy, orange-bitters, and similar drinks are also of the nature of cordials. These preparations do not require detailed description.

ABSINTHE is a liqueur containing a somewhat variable proportion of real alcohol, and several units of volatile oils,—those of cinnamon, cloves, anise, and angelica being frequently employed. Its characteristic constituent, however, is the oil of worm wood (*Artimisia absinthium*), to which the highly deleterious properties of absinthe are probably attributable. In consequence of the presence of essential oils, absinthe becomes milky on addition of water. Some varieties of absinthe contain little or no sugar. The following table shows the amounts of alcohol and essential oils contained in four different brands of absinthe. The figures are due to Adrian, and are expressed in terms of a glass of 30 c.c. of the liqueur :—

	Absolute Alcohol.	Oil of Wormwood.	Total Essential Oils.
Ordinary absinthe . . .	14·3 c.c.	·005 grammes	·030 grammes
“Demi-fine” „ . . .	15·0 „	·010 „	·046 „
“Fine” „ . . .	20·4 „	·010 „	·085 „
Swiss „ . . .	24·2 „	·010 „	·085 „

Absinthe nearly always has a faintly acid reaction, which is probably due to acetic acid. It usually amounts to 1·5 grammes of acetic acid per litre. The green colour of absinthe ought to be due to chlorophyll, introduced from spinach or parsley. A mixture of sulphate of indigo with picric acid or

turmeric is not unfrequently employed, and salts of copper have also been used. Copper can be readily detected by diluting the liqueur and adding potassium ferrocyanide, which will occasion a brown colour. The vegetable colouring-matters are perhaps best detected by their absorption spectra. Picric acid may be recognised by diluting the liqueur with weak sulphuric acid, and shaking with ether, which will acquire a yellow colour and will dye silk yellow.

The alcohol contained in absinthe may be determined by the ordinary process of distillation, the proportion of essential oils being insufficient to affect the density materially. For the determination of the essential oils, Baudrimont recommends that the distilled liquid should be somewhat diluted to cause the oils to separate, and then shaken twice with carbon disulphide. This being removed from the bottom by a tap, and allowed to evaporate spontaneously, leaves the essential oils.

NOYEAU has a flavour which is sometimes due to hydrocyanic acid, and in other cases to oil of bitter-almonds, or to nitrobenzene. (See Kirschwasser, page 105.)

**Tinctures.**—In medicine, various alcoholic solutions are employed, their permanency rendering them very convenient. These solutions are called "tinctures" or "spirits." In some cases they are directed to be prepared with "Rectified Spirit, B.P." (sp. gr.  $\cdot 835 = 84$  per cent. by weight of absolute alcohol). The tinctures and spirits of chloroform, ether, aconite, ferric chloride, ferric acetate, iodine, myrrh, nux vomica, camphor, ginger, &c., are made in this way. On the other hand, "Proof Spirit, B.P." (sp. gr.  $\cdot 920$ ) is directed to be used in making the tinctures of orange-peel, belladonna, cantharides, catechu, digitalis, ergot, opium, rhubarb, squills, &c.

There are in most cases good reasons for the choice of the above strengths of spirit, as experience has shown them to be the best adapted for the solution of the active principles of the respective drugs.

As, in the preparation of the above tinctures, proof spirit is sometimes substituted for rectified spirit, and a mixture of equal measures of rectified spirit and water for proof spirit, it is sometimes required to ascertain the strength of the alcohol which has been employed.

Mere distillation is sufficient to separate the alcohol from the tinctures of aconite, arnica, belladonna, calumba, capsicum, catechu, jalap, nux vomica, opium, quinia, &c.; and the same is true of the tinctures of iodine, ferric acetate, &c., if they be first treated with soda in slight excess. On the other hand, the tinctures of benzoin, myrrh, ginger, camphor, rhubarb, &c., give a distillate contaminated with essential oils or similar volatile matters in quantity sufficient to affect seriously the determination of the alcohol by the density. The same is true of the "aromatic spirit of ammonia," and tinctures prepared with it, with the additional objection that the distillate will contain ammonia, unless the alkaline reaction of the spirit be previously carefully neutralised by hydrochloric acid.

Spirits of chloroform, nitrous ether, and ether will, of course, yield distillates requiring special examination, or they can be examined directly. In the other tinctures to which the distillation process is not directly applicable, the alcohol may be determined in the following manner:—50 c.c. are taken and made up to 350 c.c. by addition of water. This usually causes a precipitation of the volatile oils or resinous matters, owing to their insolubility in water or very dilute alcohol. The liquid cannot be directly filtered, owing to the fine state of division in which the precipitate exists, but it may be clarified by adding a few drops of a strong solution of calcium chloride, followed by some sodium phosphate. The resultant precipitate of calcium phosphate entangles the oily and resinous matters. The liquid is now made up to 400 c.c., filtered through a dry filter, and 250 of the filtrate distilled at a low temperature, and the density of the distillate observed after being made up to 250 c.c. by means of water. If the foregoing instructions



be adhered to, the percentage of proof-spirit corresponding to the density of the distillate, multiplied by 8, will be the percentage by volume of proof-spirit contained in the tincture. The percentage of absolute alcohol by weight corresponding to this amount will be the percentage of alcohol contained in the spirit of the tincture.

This is the most convenient mode of expressing the alcoholic strength of tinctures, as it gives a figure which should approximate to the percentage by weight of absolute alcohol in the spirit used for making the tincture. Close accordance is not to be expected, for many of the drugs used contain water, and in other cases they sensibly increase the volume of the liquid.\* In deciding on the strength of the alcohol employed in making the tincture, the nature of the other ingredients should be carefully considered, and, when possible, a similar tincture should be made up with alcohol of known strength, and analysed in a similar manner to the sample.†

\* Spirit of camphor has a volume equal to the sum of the measures of the camphor and alcohol used in preparing it.

† A good example of the mode of examining a tincture is afforded by the "compound tincture of camphor," B. P., a remedy largely employed by the medical profession, and commonly known to the public by the obsolete name of "Paregoric Elixir." This preparation consists of a solution of 40 grains each of opium and benzoic acid, 30 of camphor, and half a fluid drachm of oil of anise, dissolved in proof-spirit, and diluted with the same to one pint. The spirit being the most costly ingredient, there is a strong inducement to the vendor to reduce its amount, a practice which necessitates the omission of a portion of some of the other ingredients. On diluting genuine compound tincture of camphor the major part of the oil of anise is precipitated, and if the diluted liquid be then treated with calcium chloride and excess of sodium phosphate, filtered, rendered distinctly alkaline, and distilled, the alcohol is obtained in a state of approximate purity. The small quantity of camphor present in the original tincture passes over with the spirit, and modifies the density of the product to a slight extent; the difference is unimportant. In the case of compound tincture of camphor, the treatment with calcium chloride is not strictly necessary, as the proportion of oil of anise is very small, but carbonate of sodium should be added to fix the benzoic acid. The "extract" from the distillation should be concentrated to a small bulk, and strong hydrochloric acid added in excess. This should cause a precipitation of benzoic acid, and on shaking the liquid with ether, removing the upper liquid with a pipette, and evaporating off the ether by a current of dry air, the benzoic acid is obtained in a state of approximate purity and in a state fit for weighing. Sometimes the benzoic acid is wholly omitted from the compound tincture of

If from any cause, such as the appearance or smell of the distillate, there be doubt as to the freedom of the alcohol from matters liable to affect its gravity, the distillate may be examined by Monell's colorimetric method (see page 92).

Occasionally, tinctures are fraudulently prepared with methylated spirit. The substitution may be detected by the methods described on page 71, *et seq.*

## AMYL ALCOHOL.

**Amylic Hydrate. Potato-spirit.**  $C_5H_{12}O = C_5\frac{H_{11}}{H} \} O.$

—Several amylic alcohols are known, differing somewhat in their physical and chemical properties. Normal amyl alcohol boils at 135° C. Iso-amyl alcohol boils at 128° to 132° C., and has a density of .8148 at 14° C. This is the variety of amyl hydrate produced by fermentation, and therefore present in fusel oil, and all subsequent statements respecting amyl alcohol have reference to this body.\*

Pure amylic alcohol is a colourless liquid of peculiar odour and burning taste. Dropped on paper it produces an oily mark which disappears slowly.

One part of pure amylic alcohol dissolves in 39 parts of water at 16.5° C., forming a liquid of .998 specific gravity. One part of water dissolves in 11.6 parts of amylic alcohol, forming a clear liquid of .835 specific gravity.

camphor. The same remark applies to the oil of anise, more than traces of which cannot be present if the tincture remains clear when diluted with three or four times its measure of water. The proportion of opium present in compound tincture of camphor can be judged of by the depth of red colour produced when the sample (previously diluted with water or proof spirit) is treated with ferric chloride. By comparing the tint obtained with that given by a similar tincture of known quality, a fair criterion of the proportion of opium may be obtained.

\* Normal amyl alcohol has a constitution expressed by the formula  $CH_2CH_2CH_2CH_2CH_2OH$ . Iso-amyl alcohol—the amyl alcohol of fermentation—is thus constituted:  $CH_2CH(CH_3)_2CH_2OH$ . Several secondary amyl alcohols are known, and Chapman (*Journ. Chem. Soc.* xx. page 495) has given some evidence to show that one of them is sometimes present in fusel oil. Rabuteau has found one of them (methyl-propyl-carbinol),  $CH_3C_3H_7 \cdot CHOH$ , in potato fusel oil. See note, page 117.

Amylic alcohol is miscible in all proportions with ethyl alcohol, ether, chloroform, benzene, petroleum spirit, and fixed and volatile oils.

Amylic alcohol dissolves in all proportions in glacial acetic acid diluted with an equal bulk of water, and may thus be separated from neutral amylic ethers (*e.g.*, acetate, valerate, and pelargonate of amyl) which are not soluble in acetic acid.

Amylic alcohol is very injurious. A few drops will produce all the intoxicating effects of a large quantity of ethyl alcohol, with giddiness, nausea, and other unpleasant symptoms. In larger doses it proves fatal. To its presence in new whisky the injurious effects of that spirit are attributable. On keeping the spirit, most of the amyl alcohol becomes changed or oxidised, and the injurious effects are less evident. According to the experiments of Rabuteau, amylic alcohol produces intoxicating effects of a similar kind to those due to ethyl alcohol, but 15 times as intense. (The effects of butyl alcohol were only 5 times as intense.)

The following chemical tests are of service for the  
DETECTION OF AMYLIC ALCOHOL.

1. When warmed with  $1\frac{1}{2}$  to 2 times its volume of strong sulphuric acid, amyl-sulphuric acid,  $C_5H_{11}HSO_4$ , is formed, with production of a red colour. Amyl-sulphuric acid is viscid, soluble in water and alcohol, and decomposed by distillation. In presence of sugar and other fixed substances this test is very fallacious, but if applied to a product of distillation, especially if boiling between  $120^\circ$  and  $135^\circ C.$ , the production of even a faint red colour is strong presumptive evidence of the presence of amyl alcohol.

2. When heated with an acetate and strong sulphuric acid, amyl acetate is formed (see page 159), which when perfectly pure has the odour of the jargonelle pear. In presence of  $\frac{1}{30}$ th part of ethyl alcohol, the product smells of the bergamot pear.

3. When amylic alcohol is heated with an oxidising agent,

*e.g.*, sulphuric acid and bichromate of potassium, an apple-like odour of valeric aldehyde,  $C_5H_{10}O$ , is first produced, followed by the strong and peculiar smell of valeric acid,  $HC_5H_9O_2$ . If desired, the valeric acid may be distilled off and determined. This method is adopted for the detection of amyl alcohol in spirituous liquids (see page 122). In presence of much ethyl alcohol, the smell of the resultant acetic acid quite overpowers the valeric acid.

THE DETERMINATION OF AMYL ALCOHOL may be approximately effected by oxidising it to valeric acid by dilute chromic acid mixture as described on page 93. In the absence of other acid-yielding substances, the valeric acid may be determined by titration. In other cases the method described on page 122 must be resorted to.

The determination of amyl alcohol in spirituous liquids is based on the above principles (see page 122).

The separation of amyl alcohol from moderate quantities of ethyl alcohol is fully described under fusel oil (see page 119).

From butyl alcohol and valeric aldehyde (boiling at  $93^{\circ}C$ .), amylic alcohol is approximately separated by fractional distillation (see next page).

From neutral amylic ethers, amylic alcohol may be separated by agitation with glacial acetic acid diluted with an equal bulk of water,—a liquid in which the ethers are insoluble.

**Fusel Oil.**—In the alcoholic fermentation of potatoes, corn, and the marc of grapes, there are always formed,—and especially when the fermentation is conducted in an alkaline, or but slightly acid, liquid,—in addition to common alcohol, various oily bodies of higher boiling points than alcohol, and which are, therefore, found in the last portions of the distillate obtained in the process of rectification. These liquids consist chiefly of alcohols of the series  $C_nH_{2n+2}O$ , and together constitute “fusel” or “fousel oil.”

Potato fusel oil sometimes consists almost entirely of ethylic



and amylic alcohols,\* the latter forming the larger proportion. Fusel oil from other sources often contains propylic, butylic, and hexylic alcohols, and various aldehydes and ethers are frequently present.

Amylic alcohol may be separated in a state of approximate purity from fusel oil, by agitating it with strong brine, distilling the insoluble portion, and collecting the liquid which passes over between 125° and 140° C. The reason of this precaution will be evident on reference to the following table showing the boiling points of the alcohols present in fusel oil.

	Formula.	Boiling Point, ° C.
Ethyl alcohol,	$C_2H_5, OH$	78·4
Propyl alcohol,	$C_3H_7, OH$	96
Iso-butyl alcohol,	$C_4H_9, OH$	110
Iso-amyl alcohol,	$C_5H_{11}, OH$	128–132
Iso-hexyl alcohol,	$C_6H_{13}, OH$	150
Iso-heptyl alcohol,	$C_7H_{15}, OH$	165

The portion of the liquid which distils over between 105° and 115° C. consists almost entirely of iso-butyl alcohol.

The amylic alcohol obtained in the above manner may be further purified by agitating it with hot milk of lime, drying it with chloride of calcium, and rectifying and collecting separately the portion which distils at 128 to 132° C.

\* The following are proportions of various alcohols, &c., found by Rabuteau (*Compt. Rend.* lxxxvii. 501) in 1 litre of potato fusel oil :—

	Boiling Point. ° C.	Quantity.
Iso-propyl alcohol . . . . .	85	150 c.c.
Propyl alcohol . . . . .	97	30 „
Iso-butyl alcohol . . . . .	109	50 „
Normal butyl alcohol . . . . .	106·9	65 „
Methyl-propyl carbinol . . . . .	120	60 „
Iso-amyl alcohol . . . . .	128–132	275 „
Products boiling above 132° and retaining amyl alcohol }	...	170 „
Water . . . . .	100	125 „
Ethyl alcohol, aldehyde, and ethyl acetate . . . . .	...	75 „

Trimethyl-carbinol also appears to be present. No mention is made of the presence of compound ethers.

For the mode of separating amylic alcohol from the neutral ethers and aldehydes of fusel oil, see page 117.

Fusel oil may be imported into England free of duty if it contain less than 15 per cent. of proof spirit. It is tested by the Excise by shaking it with an equal volume of water to remove the spirit, and then ascertaining the amount of alcohol contained in the aqueous liquid by taking its specific gravity. The test gives erroneous results, as fusel oil is a mixture of various alcohols, of which only amylic is approximately insoluble in water. As an improvement on this test, G. L. Ulex\* recommends the following, based on the low temperature at which ethyl alcohol distils:—100 c.c. of the sample are heated in a retort till 5 c.c. have passed over; the distillate is shaken with an equal volume of a saturated solution of common salt, and the mixture allowed to stand. If the fusel oil which separates amounts to one-half of the distillate or more, the sample is sure to contain less than 15 per cent. of spirit, and is free from any fraudulent admixture with the same. If less fusel oil or none at all separate, the presence of 15 per cent. of the spirit may be safely assumed. In the latter case, the quantity of the adulterant may be determined by shaking a known measure of the sample with an equal bulk of a saturated solution of common salt (in which propyl and butyl alcohols are much less soluble than in water), allowing the aqueous liquid to settle out, distilling it, and estimating the contained alcohol by noting the volume and density of the distillate.

The author has proved the accuracy of another method of approximately separating amylic from ethylic alcohol, which is to agitate the sample in a graduated tube with an equal volume of benzene or petroleum spirit, subsequently adding sufficient water to cause the benzene to separate. The increase in the volume of the benzene indicates with approximate accuracy the amount of amylic alcohol in the sample under examination.

\* *Neues Jahrb. der Pharm.* xxxix. 333.

### Detection of Amylic Alcohol in Spirituous Liquids.

—Amylic alcohol occurs to a greater or less extent in many varieties of commercial alcohol, especially those obtained by the fermentation of grain or potatoes. To its presence in recently manufactured whisky, the deleterious effects of the raw spirit are attributable. On keeping, the amylic alcohol is more or less destroyed by oxidation and conversion into comparatively harmless ethers.

The actual proportion of amylic alcohol present in different varieties of whisky is very uncertain, but few accurate experiments having been made. According to Dupré, a sample of Scotch whisky contained .19 of amylic alcohol for 100 of ethylic alcohol. A sample of "Cape Smoke" contained .24, and of "Common Samshoe" .18 of amyl alcohol per 100 of ethyl alcohol.

The alleged adulteration of whisky with fusel oil is probably based on an error, though it is quite possible that it has occurred in exceptional cases. The natural variation in the proportion of amylic alcohol contained in spirit is very considerable, being materially affected by the mode of distillation, in addition to the causes previously mentioned.

Of the many methods of detecting amylic alcohol in spirituous liquids, comparatively few have any value. The following have all been tried by the author, and verified to the extent stated:—

1. A useful rough test is to pour the sample of spirit on filter paper contained in a plate or flat basin, allowing it to evaporate spontaneously, or by the application of a very gentle heat. In the last portions the smell of fusel oil is often distinctly recognisable, especially if the liquid be warmed. A sample of gin to which  $\frac{1}{2000}$  of amyl alcohol had been added, was found by the author to respond to this test.

2. Another useful indication is afforded by dissolving 1 gramme of caustic potash in 150 c.c. of the spirit, evaporating the liquid slowly down to 15 c.c., and then mixing it with an

equal measure (15 c.c.) of dilute sulphuric acid, when the liquid will exhale an odour which is often characteristic of the origin of the spirit, and indicative of its source in raw grain, malt, potatoes, rye, arrack, &c. The odour produced is often very disgusting.

3. A valuable means of concentrating the fusel oil is to distil off the greater part of the alcohol at as low a temperature as possible. In the residual liquid, the fusel oil may often be detected by the smell, especially while it is warm. The residual liquid is mixed with an equal measure of ether, and then well shaken. If the ethereal layer do not separate spontaneously, an equal measure of water should be added. The ethereal layer is removed with a pipette, and allowed to evaporate spontaneously. In the residue, amylic alcohol may be recognised by its smell and chemical characters. Very volatile petroleum spirit may sometimes be advantageously substituted for the ether, as, owing to its slight solubility in alcohol, it may often be applied to the original liquid.

Betelli directs the dilution of 5 c.c. of the spirit with 6 or 7 volumes of water, 15 or 20 drops of chloroform being next added, and the whole shaken strongly and allowed to stand. The deposit of chloroform is then collected and allowed to evaporate spontaneously. By pouring the mixed liquid through a wet filter, the author found he could get rid of the ordinary alcohol and water, while the amylic alcohol was retained by the chloroform, which rapidly evaporated, and left the fusel oil in a state readily recognisable by the smell. The amylic alcohol in a gin, to which  $\frac{1}{2000}$  had been purposely added, was readily recognised by the author, both by the use of ether and of chloroform.

The amylic alcohol having been separated from the ethylic alcohol by one of the above solvents, the chemical tests given on page 116 may be applied. The sulphuric acid reaction is valueless in presence of sugar, and should therefore be applied, when practicable, to a product of distillation.



THE DETERMINATION OF FUSEL OIL IN SPIRITS can only be effected very roughly. Such a result may be obtained by the application of the foregoing methods of concentration and extraction. An accurate determination is not to be expected, as fusel oil is not a definite substance, but a very variable mixture of amylic, butylic and other alcohols, various amylic ethers, &c.

1. A process, based on the determination of the amylic alcohol, has been devised by Dr Dupré, and is carried out as follows:—

An amount of spirit (previously distilled if necessary) containing 1 to 2 grammes of alcohol, is oxidised in a closed flask with 100 c.c. of the chromic acid solution described on page 93, the rest of the process being conducted exactly as there detailed. The acid distillate is then neutralised with normal solution of soda, the solution evaporated to a small bulk, and transferred to a retort. An amount of normal sulphuric acid equal to  $\frac{1}{20}$ th of the normal soda previously employed is next added, and the contents of the retort distilled to dryness on an oil-bath at a temperature of about 130° C. Another addition of acid to the same extent as before is now made, some water added, and the distillation repeated. It is well to distil to dryness once or twice more with water only. The acid distillate contains all the valeric, butyric, and other acids producible from the fusel oil present in the spirit, the greater part of the acetic acid resulting from the oxidation of ethyl alcohol remaining in the retort as sodium acetate. The distillate is next neutralised by boiling it with pure precipitated barium carbonate,\* filtered, evaporated to dryness, the residual barium salts dried at 130° C., and weighed. By subsequently converting the product into barium sulphate (by moistening the residue with sulphuric acid, and again igniting), the necessary data for ascertaining the proportion of amylic

\* The barium carbonate may be advantageously replaced by using a slight excess of baryta water, then passing carbonic acid, and boiling well.

alcohol are obtained. For the mode of calculation see page 218. From the composition of the mixed barium salts thus ascertained, the proportion of amylic and ethylic alcohols may be calculated. Of course, by the fractional saturation of the alkali by sulphuric acid, an amount of acetic acid equivalent to  $\frac{9}{10}$ ths of the total normal alkali used was retained in the retort. This additional amount must be calculated into ethyl alcohol ;

60 parts of acetic acid correspond to 46 of ethyl alcohol.
102        „        valeric                        „        88 of amyl alcohol.

Instead of calculating the proportion of valeric acid from the composition of the barium salts, the amount may be ascertained by Duclaux' method (see page 212). Or the two methods may be combined by redissolving the barium salts in water, precipitating the liquid with a slight excess of dilute sulphuric acid, filtering off, and weighing the  $\text{BaSO}_4$ . The filtrate is diluted to 110 c.c., 100 c.c. distilled off, and each fraction of 10 c.c. titrated, as described on page 213.

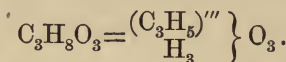
2. When the proportion of fusel oil is considerable, the amount may be approximately ascertained by distilling 500 or 1000 c.c. of the spirit. When the thermometer rises to  $98^\circ$  the receiver is changed, and the portion distilling between that temperature and  $110^\circ$  collected separately and again fractionally distilled. The last portion so obtained is added to the part of the first distillate coming over between  $110^\circ$  and  $135^\circ$  C. These united distillates are set aside ; after the first hour or two, if no aqueous layer separates at the bottom,  $\frac{1}{4}$ th of the volume of water is added, and the whole agitated. After twelve hours, the aqueous layer is removed with a pipette and the residual fusel oil weighed. During the distillation the temperature should be carefully watched, and not allowed to much exceed  $135^\circ$  C., or the distillate may be contaminated with empyreumatic products. This process aims at the direct determination of the fusel oil as such, instead of the estimation of any leading constituent. Pro-

bably the method might be advantageously modified by agitating the fusel oil distillate in a graduated tube with an equal volume of benzene or petroleum spirit, and estimating the amount of fusel oil from the increase in the bulk of the upper layer.

## GLYCERIN.

### Glycyl Alcohol.

*French*—Glycérine.



Glycerine is a product of the decomposition of fatty bodies by bases or by water at high temperatures. It is also a constant product of the alcoholic fermentation, and hence is a natural constituent of wine, beer, and other fermented liquids.\* In its chemical relationships it is a triatomic alcohol.

Pure glycerin is a colourless, viscid liquid, without odour, but having an intensely sweet taste. It is without action on polarised light. It is not readily frozen, but large crystals are obtainable when a sample of very pure glycerin is long exposed to great cold. Glycerin is volatile without change in a vacuum, but when distilled under the ordinary atmospheric pressure it suffers partial decomposition, with formation of acrolein,  $\text{C}_3\text{H}_4\text{O}$ , acetic acid, and other products. Pure glycerin has a density of 1.266 at  $15^\circ\text{C}$ ., and boils at  $290.9^\circ\text{C}$ .

Glycerin does not volatilise at ordinary temperatures. It is miscible with water in all proportions, with corresponding decrease of viscosity and density.

The density of the glycerin of the British Pharmacopœia is 1.25, which corresponds to an admixture of about 5 per cent. of water.

Tables showing the proportions of glycerin and water contained in mixtures of various densities have been constructed

\* Glycerin is not unfrequently *added* to wine and beer.

by Champion and Pellet, Fuchs, and Schweikert. The two latter agree closely in their results, but the first observers differ from them somewhat. All, however, agree that the density of glycerin proceeds very regularly with the dilution. Hence a formula can be conveniently substituted for the table. The following formulæ give results agreeing closely with the observed specific gravities of diluted glycerin, as given by Fuchs and by Schweikert.  $d$  is the density of the sample compared with water at  $15^{\circ}\text{C.}$  ( $=59^{\circ}\text{F.}$ ). Then—

$$\frac{1266 - 1000d}{2.66} =$$

The percentage of water by volume contained in the sample; and

$$\frac{1266 - 1000d}{2.66d} =$$

The percentage of water by weight contained in the sample.

The co-efficient of expansion of glycerin is .0006 for a rise of temperature from  $15^{\circ}$  to  $16^{\circ}\text{C.}$

Glycerin is miscible in all proportions with alcohol, but is insoluble in chloroform,\* benzene, petroleum spirit, carbon disulphide, or fixed oils. Glycerin is nearly insoluble in ether, from which it separates any alcohol or water. It is soluble in a mixture of two volumes of absolute alcohol and one volume of ether—a fact which may be employed to separate it from sugar, gum, gelatin, &c. Another useful solvent of glycerin is a mixture of equal weights of chloroform and alcohol, in which liquid sugar, dextrin, gum, and many extractives are insoluble.

Glycerin is without action on litmus, and is not very readily acted on by reagents. Strong nitric acid converts it into glyceric acid,  $\text{C}_3\text{H}_6\text{O}_4$ , or into nitro-glycerin (see page 131). With sulphuric acid, glycerin produces sulphoglyceric acid,  $\text{C}_3\text{H}_8\text{O}_3\text{SO}_3$ , which forms soluble barium, calcium, and lead salts.

\* The statement made in *Watt's Dictionary*, vol. ii. page 889, on the authority of Palm, that chloroform may be employed for the separation of sugar and glycerin, I have found to be incorrect. Chloroform, if free from alcohol, has no solvent action on glycerin.—A. H. A.



By the action of acids in sealed tubes, glycerin yields various glycerides or glycylic ethers, which are for the most part oily liquids, increasing in viscosity as the acid radical contained in them has a higher combining weight. Those formed from the higher acids of the fatty series (*e.g.*, palmitic and stearic acids) are solid fats.

By the action of iodide of phosphorus, glycerin yields iodide of allyl,  $C_3H_5I$ .

When glycerin is heated with a dehydrating agent (*e.g.*, concentrated sulphuric acid), irritating fumes of acrolein,  $C_3H_3O,H$ , are evolved, smelling of burning fat.

Glycerin has very considerable solvent properties, and acts as an antiseptic, even when largely diluted. It is not readily inflammable, but may be burnt from a wick like alcohol. Pure glycerin, when heated in a porcelain crucible till it catches fire, and then allowed to burn away, leaves a mere trace of carbonaceous residue. Any considerable black residue indicates serious impurity. An incombustible residue may consist of salts of calcium, sodium, or lead.

THE DETECTION OF GLYCERIN IN ORGANIC LIQUIDS is most readily effected by the following method proposed by Senier and Lowe. According to these authors, the only substances giving a similar reaction are glycol,  $C_2H_4(OH)_2$ , and erythrite. The solution to be examined is made slightly alkaline with dilute solution of soda, and a bead of borax (made by fusing the salt on a loop of platinum wire) dipped into it. The bead is allowed to rest for a few minutes, so as to allow solution to take place on its surface, and is then held in the flame of a Bunsen burner. A more delicate plan is to place some powdered borax in a watch-glass, pour on it some of the faintly-alkaline liquid to be tested, and, by means of a looped platinum wire, introduce some of the mixture into the flame. In either case a deep-green flame will be produced, if even a small quantity of glycerin be present. The reaction becomes indistinct if the liquid contains less than 5 per cent.

of glycerin. For detecting glycerin in beer, wine, milk, &c., 50 or 100 c.c. of the liquid should be evaporated to dryness on the water-bath, the residue extracted with absolute alcohol, the solution so obtained again evaporated, and the resultant residue moistened with a few drops of water and tested with borax, as above described. Ammonium salts give a similar reaction to glycerin. When present, they must be thoroughly got rid of by evaporating the original liquid with sodium carbonate. The test experiments of Messrs Senier and Lowe are very satisfactory, but the author has but little personal experience of the reaction.

THE DETERMINATION OF GLYCERIN IN COMPLICATED ORGANIC LIQUIDS presents great difficulties, which are in some cases insuperable in the present imperfect state of proximate analysis. Many admixtures may be got rid of by precipitating the solution with basic acetate of lead, and subsequently removing the excess of lead from the solution by sulphuretted hydrogen. This method may be employed for the analysis of the B. P. preparations called "glycerin of tannic acid" and "glycerin of gallic acid." It is also applicable to the determination of glycerin in soap, if, after treatment with sulphuretted hydrogen, the liquid be evaporated as far as possible on the water-bath, and the residue extracted with a mixture of two volumes of absolute alcohol and one of ether, when the glycerin is dissolved, and may be recovered by evaporating off the solvent, and ultimately weighed.

According to Moffit, the glycerin in soap can be determined by dissolving 10 grammes of the sample in alcohol, precipitating the bases as sulphates (all sulphates are insoluble in alcohol) by addition of sulphuric acid diluted with alcohol, filtering, adding barium carbonate in excess, filtering again, and evaporating the sweet filtrate till free from alcohol. The resultant glycerin can either be concentrated and weighed, or its volume may be accurately noted, and the quantity of glycerin calculated from its density in a dilute state.

For the determination of glycerin in wine and beer various methods have been proposed, but none of those of which the author has experience are very satisfactory. They are mostly based on the precipitation of the liquid by lime or oxide of lead, evaporation of the filtrate to complete dryness, and extraction of the glycerin from the residue by a mixture of alcohol and ether or alcohol and chloroform. From the solution so obtained the glycerin is separated by evaporation at  $100^{\circ}\text{C}$ ., and subsequently weighed.

Reichart evaporates the wine to dryness with a slight excess of slaked lime, extracts the glycerin from the residue by boiling it with rectified spirit, and evaporates the filtered solution on the water-bath. With genuine wine this is said to give nearly pure glycerin; but if the wine be sophisticated, a further purification of the glycerin must be effected by dissolving it in a mixture of alcohol and ether, filtering, and evaporating the solution on the water-bath.

Pure wine contains 6 to 8 grammes of glycerin per litre. When adulterated, it may contain from 12 to 40 grammes per litre.

**Commercial Glycerin.**—Glycerin is now usually prepared by decomposing fats by super-heated steam. The glycerin is obtained by concentrating the aqueous portion of the distillate. Another method sometimes employed consists in decomposing olive oil by oxide of lead. Oleate of lead and glycerin result. Glycerin so made is very liable to contain lead as an impurity. This is best detected by dissolving the residue left on burning off the glycerin (in porcelain) in a few drops of nitric acid, and testing the diluted liquid with sulphuretted hydrogen. A black or brown coloration indicates the presence of lead. Lead may also be detected (though less certainly) by direct treatment of the diluted glycerin with sulphuretted hydrogen.

When the glycerin is a product of the saponification of olive-oil with lime, it often contains oleate of calcium.



The lime will be found in the residue left on combustion of the glycerin, or it may be detected by mixing the sample with an equal measure of alcohol and a few drops of sulphuric acid. If lime be present, a white cloud or precipitate of calcium sulphate will be produced. Oxalate of ammonium may also be employed to test for lime, the presence of which renders glycerin unfit for some medical and pharmaceutical purposes.

When glycerin is the result of the treatment of fats with sulphuric acid, it often contains calcium sulphate and foreign organic matters, due to the action of the acid on the fat at elevated temperatures. Such glycerin is unfit for certain purposes, such as the manufacture of nitroglycerin. These impurities may be detected by diluting the sample with twice its weight of water, and treating it in the cold with excess of solution of basic acetate of lead. The formation of an abundant precipitate which rapidly subsides is an indication of considerable impurity in the sample. The proportion of impurity may be found by collecting the precipitate on a tared filter, washing, and drying at  $100^{\circ}\text{C}$ . The filter and precipitate are again calcined, the residue treated with nitric and sulphuric acids, and again cautiously ignited. The residue of lead sulphate,  $\text{PbSO}_4$ , is calculated to oxide,  $\text{PbO}$ , by multiplying its weight by  $\cdot 736$ . The amount so obtained is deducted from the total weight of the lead precipitate, the difference being that of the organic matter sought. The proportion of impurity so estimated rarely exceeds 1 or 1.5 per cent. of the weight of the glycerin. In addition to the quantitative determination of the foreign organic matter by precipitation with lead, glycerin intended for the manufacture of nitroglycerin should also be assayed for the percentage of lime, water, and glycerin.

Some samples of commercial glycerin have an irritating and burning taste even when diluted. This is generally due to the presence of formic acid. This impurity is best



detected by adding ammonio-nitrate of silver to the diluted sample. On leaving the mixture for half an hour at the *ordinary* temperature, a black precipitate is produced if formic acid be present. At temperatures above  $50^{\circ}\text{C}$ ., pure dilute glycerin causes the reduction of ammonio-nitrate of silver. With neutral nitrate of silver pure diluted glycerin gives no reaction. In presence of acrolein or butyric acid, a white precipitate is produced, which blackens on standing or boiling.

By heating glycerin with rectified spirit and concentrated sulphuric acid, a more or less fruity smell is developed if formic or butyric acid be present; a pine-apple-like odour of ethylic butyrate is frequently observed.

Oxalic Acid is not unfrequently present in commercial glycerin. Such specimens cause reddening when applied to the skin, and are irritating to sores. Distilled glycerin never contains this impurity. In presence of oxalic acid, the glycerin will give a white turbidity on adding solution of calcium acetate. Concentrated sulphuric acid, mixed with an equal volume of such glycerin, becomes warm and effervesces. Other impurities cause darkening, or even charring.

German glycerin often turns light-yellow in colour when mixed with hydrocyanic acid. Pure glycerin is unaffected.

GLYCERIN INTENDED FOR MEDICINAL USE should be neutral to litmus, and unaffected by strong sulphuric acid, nitrate of silver, sulphuretted hydrogen, oxalate of ammonium, or exposure to sunlight.

THE ADULTERATION OF GLYCERIN is sometimes practised by the addition of saccharine matter, which also allows of dilution with water without great reduction of the density. Glucose may be detected by the brown coloration produced on boiling the sample with soda. It may also be detected by diluting the sample with an equal bulk of water, and heating it nearly to boiling for a few minutes with Fehling's copper solution, which will cause a yellow or red precipitate

of cuprous oxide in presence of glucose or dextrin, but has no effect on pure glycerin. Cane sugar is not indicated by either of the above tests. For its detection, the sample should be diluted and boiled for twenty minutes with a little sulphuric acid. This will cause the change of the cane sugar to glucose, and Fehling's test can then be satisfactorily applied. The determination of sugar in glycerin can be effected by the quantitative application of this well known test.

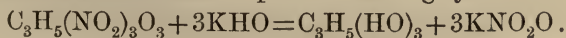
**Nitroglycerin.**—Glonoin oil.  $C_3H_5N_3O_9 = C_3H_5(NO_2)_3O_3$ .  
—When strong glycerin is cautiously added to an excess of a well-cooled mixture of fuming nitric and concentrated sulphuric acids, it is converted into tri-nitrate of glycy, or nitroglycerin. When great care is taken, almost the theoretical amount is obtainable.

Nitroglycerin is an oily liquid of 1.600 specific gravity at  $15^\circ C$ . It freezes at about  $8^\circ C$ . It *explodes* with extreme violence when smartly struck or compressed, or when dropped on a hot iron plate, but small quantities of it burn quietly when inflamed.

Nitroglycerin is slightly volatile at ordinary temperatures; the inhalation of the vapour occasions violent headache.

Nitroglycerin is almost insoluble in water, but is soluble in ether and alcohol, and very readily soluble in wood-spirit. From the two latter solutions it is reprecipitated on addition of water. This fact may be utilised for its purification, and—by subsequently titrating the aqueous liquid with standard alkali—for ascertaining the proportion of free acid in the commercial product or its preparations. The presence of free acid in nitroglycerin indicates imperfect manufacture of the sample, and a special liability to spontaneous decomposition and explosion.

Nitroglycerin is decomposed by boiling with an alcoholic solution of caustic alkali, the main reaction resulting in the formation of a nitrate and reproduction of glycerin.



In this reaction acetic and formic acids, aldehyde-resin, ammonia, &c., result as secondary products. Hence the process is not available for the quantitative assay of nitroglycerin.

Champion and Pellet\* adopt the following method of determining the  $\text{NO}_2$  of nitroglycerin. A known quantity of solution of ferrous sulphate of previously ascertained reducing power is placed in a flask, acidified with hydrochloric acid, and its surface covered with a layer of petroleum oil. About 5 grammes of the nitroglycerin is then introduced, and the flask heated on a water-bath. When the sample is completely decomposed, the liquid is heated to boiling to remove nitric oxide, and the excess of ferrous sulphate ascertained by titration with standard permanganate. 56 of Fe oxidised by the sample correspond to 23 of  $\text{NO}_2$  in the nitroglycerin.

DYNAMITE, LITHOFRACTEUR, and DUALINE are mixtures of nitroglycerin with various inert bodies. The strongest dynamite contains 75 per cent. of nitroglycerin, and 25 per cent. of burnt *Kiesel-guhr*—an infusorial earth. The proportion of nitroglycerin in such preparations may be ascertained by treating a known weight of the sample with wood-spirit, and drying and weighing the residue. The loss of weight is the nitroglycerin dissolved out. For assaying mixtures of nitroglycerin with sugar or alum, ether should be substituted for the wood-spirit; or, another very convenient but less accurate plan is to shake a known weight of the sample with water in a graduated tube, when its volume may be read off. The number of cubic centimetres found, multiplied by 1.6, gives the weight of nitroglycerin in the sample taken.

\**Compt. Rend.* lxxxiii. 707. *Journ. Chem. Soc.* 1877, i. 228.

## NEUTRAL ALCOHOLIC DERIVATIVES.

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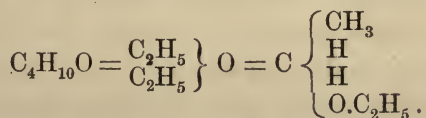
AMONG the neutral derivatives of the alcohols are included a number of important bodies, of which chloroform, ether, compound ethers, and aldehyde are prominent examples.

As a rule, the neutral derivatives of the alcohols are volatile ethereal liquids, but important exceptions exist to this generalisation. The bodies of this division employed in commerce are of too varied a nature to admit of general description. The more important of them are fully discussed under special sections devoted to them.

### ETHER.

#### Ethylic Ether. Ethyl Oxide.

*French*—Ether. *German*—Aether.



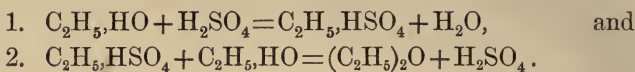
When used as a proper name the term “ether” always signifies ethylic ether. When employed generically the word ether has a far wider signification (see p. 138).

Ether can be obtained by a variation of reactions, but is always manufactured in practice by distilling alcohol with strong sulphuric acid.\* The reaction consists first in the production of ethyl-sulphuric acid (sulpho-vinic acid)  $\text{C}_2\text{H}_5\text{HSO}_4$ , and this product at a higher temperature ( $130^\circ$

\* In reference to this mode of preparation, ether was formerly called “sulphuric ether.”



C.) acts on a second molecule of alcohol with formation of ether.



It is thus evident that sulphuric acid is reproduced. Theoretically, therefore, a limited quantity of sulphuric acid is capable of converting a much larger quantity of alcohol into ether. Advantage is taken of this fact in practice, but the formation of secondary products ultimately puts a stop to the process. The first distillate contains (besides ether) alcohol, water, sulphurous and acetic acids, oil of wine, &c. By addition of water the alcohol may be eliminated, the ether forming a separate layer on the surface. The acids and water may be got rid of by agitation with potassium carbonate, and the ether obtained pure by redistillation.

Ether is a highly volatile, colourless, limpid liquid, of penetrating agreeable odour, and pungent sweetish taste. When pure, it boils at 35° C., and has a density of 0·713 at 15° C., or 0·7185 at 17·5° C.

Ether is sparingly soluble in water, and still less so in glycerin, the solutions having a neutral reaction. With alcohol, chloroform, benzene, petroleum naphtha, fixed and volatile oils, ether is miscible in all proportions.

Ether dissolves resins, fats, quinine, phosphorus, bromine, iodine, ferric, mercuric, and auric chlorides, and mercuric (but not mercurous) iodide.

In the air, ether oxidises very slowly to acetic acid. Both the liquid and vapour are very combustible.

COMMERCIAL ETHER is not very liable to intentional adulteration. It frequently contains water (1 part of water dissolves in 35 of ether) and very considerable quantities of alcohol. The presence of alcohol increases the *apparent* solubility of the sample in water, as on shaking with that solvent all the alcohol passes into solution (see page 136).

The presence of water or alcohol in ether tends to increase the gravity and raise the boiling point of the sample. Ether of density .728 contains about 5 per cent. of alcohol.

Absolute ether forms a clear mixture with any proportion of oil of copaiba. If it contain alcohol or water it forms an emulsion when shaken with a considerable proportion of the oil.

Anhydrous ether forms a perfectly clear mixture with an equal bulk of carbon disulphide. If the smallest quantity of water be present the mixture is milky.

The most delicate test for the presence of alcohol in ether is that of Lieben, founded on the formation of iodoform by alcohol but not by ether. The method of applying the test is described on page 80. Very careful purification is necessary to obtain ether which does not respond to this test, and mere keeping in presence of moisture generates traces of alcohol sufficient to produce the reaction.

Several chemists have pointed out that crystallised fuchsine (acetate of rosaniline) is insoluble in pure anhydrous ether or chloroform, but that it imparts more or less colour to these liquids when alcohol is present.

When the sample is well agitated with dry chloride of calcium to remove alcohol and water, it loses the power of dissolving fuchsine, becoming tinged only very faintly when shaken with the dye.

To employ the above facts for the determination of small quantities of alcohol in ether, the author operates in the following manner:\*

A minute quantity of powdered fuchsine is placed at the bottom of a narrow test-tube, 10 c.c. of the sample of ether added, the tube corked and the whole agitated. If the ether be pure and anhydrous, the coloration of the liquid will be almost *nil*. If the coloration be considerable, 10 c.c. of ether which has been treated with chloride of calcium is placed in

\* *Analyst*, 1877, page 97.

another tube of the same bore as the first, adding fuchsine as before.  $\frac{1}{10}$ th c.c. of alcohol is then added to it from a finely-divided burette, and the whole is shaken. If this quantity of alcohol be insufficient to produce a coloration of the liquid equal to that of the sample to be tested, a further addition of alcohol must be made until the liquids have the same depth of colour. The tint is best observed by holding the two tubes side by side in front of a window and looking through them transversely. The use of a piece of wet filter-paper behind them facilitates the observation. It is well to permit the alcohol to drop right into the ether, and not allow it to run down the sides of the tube, as in the latter case it will dissolve any adherent particles of fuchsine, forming a solution which will be precipitated on admixture with the ether. For a similar reason it is not convenient to dilute the sample with pure ether, so as to reduce the colour to that of a standard tint. In practice, each  $\frac{1}{10}$ th c.c. of alcohol added from the burette may be considered as indicating 1 per cent. of impurity in the sample. Of course this assumption is not strictly correct, but the error introduced is insignificant when the percentage of alcohol is small. The method is very suitable for small proportions of alcohol, but becomes difficult to apply when the latter exceeds 5 per cent. of the sample, owing to the intensity of the colour. The results are within  $\frac{1}{4}$  per cent. of the truth. Occasionally the tints of the two liquids are not readily comparable, but on placing the tubes for a few minutes in cold water, this difficulty is overcome.

Ether free from alcohol is soluble in ten times its measure of water. Agitation with water extracts any alcohol it may contain, and thus diminishes the volume of the ether. The method appears very unpromising in presence of much alcohol, but with certain precautions, it is possessed of considerable accuracy. The following are the details of the procedure the author has found preferable:\*

\* *Analyst*, 1877, page 98.

A small quantity of fuchsine placed in a Mohr's burette furnished with a glass tap, which is then filled with water and a small proportion of ether; a cork is next introduced, and the whole agitated. By this means a coloured etherised water is obtained, in which ether is quite insoluble, while alcohol readily dissolves.\* 10 c.c. of the etherised water are run into a glass tube holding about 25 c.c., and having divisions of  $\frac{1}{10}$  c.c., 10 c.c. of the sample of ether are next added, the tube corked, and the whole well shaken.

On the ether rising to the surface, its volume can be easily read off. Any reduction in its volume is due to admixture of alcohol. Thus each 0.1 c.c. lost, represents 1 per cent. of alcohol. If the proportion of alcohol in the sample does not exceed 20 per cent., the ether will be colourless, and the result of the experiment is correct; but if the proportion of alcohol is much above 20 per cent., the layer of ether is coloured, and the result is below the truth. The absence of colour, therefore, indicates the accuracy of the experiment. If the layer of ether be coloured, an accurate result can still be obtained by adding 5 c.c. of anhydrous ether, and again agitating. It is better, however, to dilute a fresh portion of the sample with an equal bulk of pure ether, and use the diluted sample instead of the original. By proceeding in this manner the proportion of alcohol in mixtures of that liquid with ether can be ascertained within 1 or 2 per cent. with great facility. The process has been verified up to 60 per cent. of alcohol.

In all cases the proportion of alcohol must be deduced from the reduction in the volume of the ether, and not from the increase in that of the aqueous liquid. Care must be taken to prevent any volatilisation of the ether.

**Methylated Ether.**—When methyl alcohol is heated with sulphuric acid it yields methylic ether,  $(\text{CH}_3)_2\text{O}$ , which is a gas

\* The etherised water can also be made (but less satisfactorily) by mixing 9.5 c.c. of water with 0.5 c.c. of pure ether in the graduated tube employed for the experiment, and then adding a minute quantity of fuchsine.

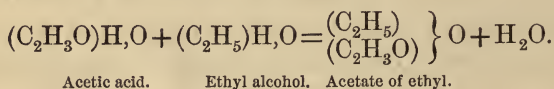


condensable only at a very low temperature. Hence, ether made from methylated spirit would be practically pure ethylic ether were it not for the presence in it of other constituents of wood-spirit. Ether prepared from methylated spirit is known as "methylated ether."

Methylated ether is said to be used as an intoxicant in the North of Ireland, and to have more than three times the stimulating effect of whisky.\*

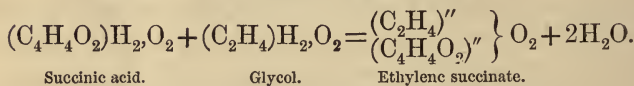
## COMPOUND ETHERS.

This term is applied to the products obtained when acids react on alcohols with elimination of water, as in the cases represented by the following formulæ:—



Acetic acid.

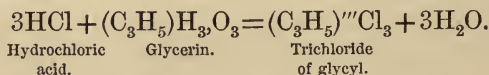
Ethyl alcohol. Acetate of ethyl.



Succinic acid.

Glycol.

Ethylene succinate.

Hydrochloric  
acid.

Glycerin.

Trichloride  
of glycyi.

Ethers may be produced in various ways, but the following general methods may be specially mentioned:—

1. By the action of the concentrated acid upon the anhydrous or concentrated alcohol containing the radical of which an ether is desired.

2. By distilling the alcohol with strong sulphuric acid and a salt of the acid of which the radical is to be introduced into the ether.

3. By dissolving the acid in the alcohol and passing hydrochloric acid gas into the liquid.

4. By reaction between the iodide of the alcohol radical the ether of which is required, and the silver-salt of the acid.

\* *Medical Press and Circular*, iv. 117.

In many respects the ethers may be regarded as true salts of the alcohol radicals, but they rarely react directly with the ordinary tests for the contained acid radicals.

As a class, the ethers are volatile solids or liquids having little solubility in water. They are frequently split up into the corresponding acids and alcohols by distillation with water (and especially by high pressure steam), and yield the alcohol and an alkaline salt when treated with caustic alkali.

The ordinary natural fixed oils and fats may be regarded as ethers, the alcohol radical being glycy l,  $C_3H_5'''$ . By treatment with alkalis or high-pressure steam, they yield glycy l alcohol (glycerin) and stearic, oleic, or other "fatty acid." The fats are examples of ethers containing a tri-atomic alcohol radical.

The detailed consideration of the fixed oils and fats may be conveniently deferred, as they form a true natural group, and do not present close physical analogies to the salts of mon-atomic alcohols, to which the term "ether" was originally, and with greater propriety, applied.

The ethers of diatomic alcohol radicals have received few practical applications, and do not require special description.

The ethers of monatomic alcohol radicals form a very extensive and interesting series of bodies having the general characters already detailed. Some of them, as the nitrites of ethyl and amyl, and the acetate of ethyl, are employed in medicine, some in perfumery, others in the manufacture of coal-tar dyes, and many others are used in the compounding of artificial fruit essences. (See page 161.)

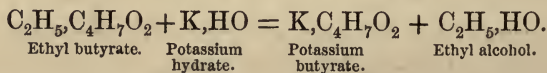
The following is a tabular list of the chief compound ethers of which practical application is made.\* The more important, and such as sometimes require chemical examination, are

\* In addition to the above, the salts of ethyl-sulphuric and ethyl-disulpho-carbonic acids are employed, and are described in separate sub-sections on page 148, *et seq.*

described in detail under separate sub-headings, on page 144, *et seq.*

Name.	Formula.	Sp. gr. at 15° to 18° C.	Boiling Point °C.	Remarks.
Methyl Acetate .	$\text{CH}_3, \text{C}_2\text{H}_3\text{O}_2$	·919	56·3	Readily soluble in water.
„ Salicylate .	$\text{CH}_3, \text{C}_7\text{H}_5\text{O}_3$	1·18	222·	Oil of winter-green. Violet colour with ferric chloride.
„ Chloride .	$\text{CH}_3, \text{Cl}$	...	-23·	Gaseous at ordinary temperatures.
„ Iodide .	$\text{CH}_3, \text{I}$	2·23	43·8	Turns brown in the light.
Ethyl Formate .	$\text{C}_2\text{H}_5, \text{CHO}$	·919	54·	Odour of peach-kernels.
„ Acetate .	$\text{C}_2\text{H}_5, \text{C}_2\text{H}_3\text{O}_2$	·898	74·	Fragrant odour.
„ Butyrate .	$\text{C}_2\text{H}_5, \text{C}_4\text{H}_7\text{O}_2$	·902	119·	Odour of pine-apples.
„ Valerate .	$\text{C}_2\text{H}_5, \text{C}_5\text{H}_9\text{O}_2$	·866	133·	Odour of valerian.
„ Pelargonate .	$\text{C}_2\text{H}_5, \text{C}_9\text{H}_{17}\text{O}_2$	·860	218·	Odour of French brandy.
„ Benzoate .	$\text{C}_2\text{H}_5, \text{C}_7\text{H}_5\text{O}_2$	1·051	213·	Fragrant odour.
„ Nitrite .	$\text{C}_2\text{H}_5, \text{NO}_2$	·947	18·	Odour of apples.
„ Nitrate .	$\text{C}_2\text{H}_5, \text{NO}_3$	1·112	86·	Sweet; hot vapour is explosive.
„ Chloride .	$\text{C}_2\text{H}_5, \text{Cl}$	1·370	11·	Burns with smoky green-edged flame producing HCl.
„ Bromide .	$\text{C}_2\text{H}_5, \text{Br}$	1·40	40·7	Burns with green-edged flame without smoke.
„ Iodide .	$\text{C}_2\text{H}_5, \text{I}$	1·946	72·	Turns brown in light, liberating iodine.
Amyl Acetate .	$\text{C}_5\text{H}_{11}, \text{C}_2\text{H}_3\text{O}_2$	·876	140·	Odour of jargonelle pears.
„ Butyrate .	$\text{C}_5\text{H}_{11}, \text{C}_4\text{H}_7\text{O}_2$	·852	170·	Fragrant odour.
„ Valerate .	$\text{C}_5\text{H}_{11}, \text{C}_5\text{H}_9\text{O}_2$	·864	188·	Odour of apples.
„ Nitrite .	$\text{C}_5\text{H}_{11}, \text{NO}_2$	·877	95-100	Orange vapour when boiled.
„ Chloride .	$\text{C}_5\text{H}_{11}, \text{Cl}$	·874	101·	Burns with luminous green flame producing HCl.
„ Iodide .	$\text{C}_5\text{H}_{11}, \text{I}$	1·509	147·	Faint odour; turned brown by light.

A general process for the analysis of compound ethers is based on their reaction with alcoholic potash or soda, which decomposes them with production of alcohol and formation of a salt of the alkali-metal, as in the following example:—



The following are the details of the process:—

A. solution of caustic potash is made in pure rectified spirit. The strength may be 6 or 8 per cent. of real KHO. It may be kept without alteration for a week or two. For use, a 50 c.c. flask with a very narrow neck is filled with the solution, a constant temperature being employed. It is best to set the

solution at the time of use by careful titration with standard sulphuric acid, subsequently using an equal quantity of alkali for the analysis.

The alcoholic solution is placed in a small flask, and from 4 to 6 grammes of the ether added, in such a way as to avoid loss. A weighed quantity contained in a small glass bulb may be employed, or a known quantity of the ether dissolved in pure alcohol may be added. An inverted Liebig's condenser is then adapted to the flask, which is heated on the water-bath for about an hour. The disappearance of the characteristic smell of the ether is a good criterion of the completion of the process. In special cases, the reaction can be effected in a sealed tube,\* but this is rarely necessary. When the decomposition is complete, the contents of the flask are rinsed out with water into a porcelain basin and titrated with standard acid. The difference between the amount of acid employed originally, and after digestion of the alkaline solution with the ether, represents the amount of acid in the ether in terms of sulphuric acid. In other words, each c.c. of *difference* between the normal sulphuric acid *originally* and *ultimately* employed, represents *one equivalent in milligrammes* of the ether present.

As many of the organic acids do not redden litmus very strongly, it is desirable to make the end of the titration the *utmost point of distinct alkaline reaction*, rather than the first distinct redness. It is probable that other indicators might be advantageously substituted for litmus in this process.

The above method of decomposing ethers with alcoholic alkaline solutions often furnishes valuable evidence of the purity of the substances examined. Thus an elementary combustion will scarcely detect 10 per cent. of ethyl alcohol in ethyl acetate, or of amyl alcohol in amyl acetate, but the above process would indicate the impurity with certainty.

After decomposing the compound ether with alkali as above

\* Or a long-necked assay-flask, closed by a well-fitting caoutchouc stopper tied down, may be conveniently employed for the decomposition.



described, and titrating the products with standard acid, a further knowledge of the ether may be obtained in the following manner:—The free alcohol is got rid of by distilling or evaporating the slightly alkaline liquid. The residue is treated with an amount of sulphuric acid fully sufficient to doubly neutralise the alkali originally added (*i.e.*, to effect the reaction  $\text{KHO} + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{H}_2\text{O}$ ), and the liquid is distilled. The acid of the ether will be liberated, and, if volatile without decomposition, will pass more or less perfectly into the distillate, where it may be further examined, converted into a barium salt, &c.

The above method may be conveniently employed for the determination of chloroform and chloral hydrate when in alcoholic solution; the reactions being—

1. With chloroform:  $4\text{KHO} + \text{CHCl}_3 = \text{KCHO}_2 + 3\text{KCl} + \text{H}_2\text{O}$ .

2. With chloral hydrate:  $5\text{KHO} + \text{C}_2\text{HCl}_3\text{O}, \text{H}_2\text{O} = 2\text{KCHO}_2 + 3\text{KCl} + 2\text{H}_2\text{O}$ .

The first reaction requires 4 equivalents, and the latter 5 of alkali. Hence, each c.c. of *difference* in the amounts of normal sulphuric acid required will represent 29.9 milligrammes of chloroform or 33.1 of chloral hydrate.

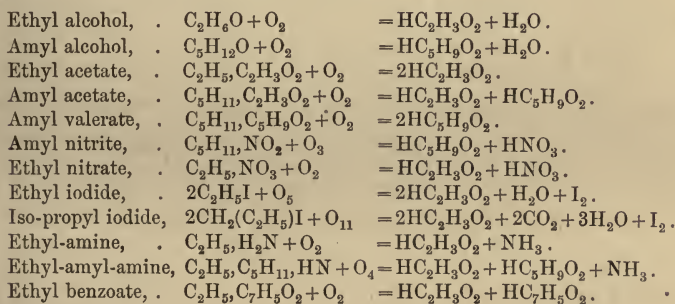
Dupré has applied the above process to the determination of the fixed and volatile ethers of wine. 250 c.c. of the wine are distilled down to about 50, and the distillate made up to 250 c.c. In 100 c.c. of this, the free volatile acid is determined by standard alkali, and another 100 c.c. is digested with a known excess of  $\frac{1}{10}$  decinormal alcoholic soda. The extent to which this is neutralised over and above that due to the free acid, represents the volatile ethers, which are best expressed in terms of acetic ether. To determine the fixed ethers (assumed to be ethyl tartrate), 250 c.c. of the wine are evaporated on a water-bath to about 40 c.c.\* The residue is distilled with

\* With wine containing much sugar the residual liquid should be diluted, and the evaporation repeated.

excess of caustic alkali, a little tannin being added to prevent frothing. The distillate contains the alcohol produced by the decomposition of the tartaric ether. It is rendered slightly acid with sulphuric acid, and again distilled, 20 c.c. being driven over. The alcohol in these 20 c.c., may be determined by the density, or preferably by the oxidation method described on page 92.

A useful general method of examining compound ethers was devised by Messrs Chapman and Smith.\* It is based on the fact that organic bodies when oxidised in a sealed tube by a mixture of sulphuric acid and acid-chromate of potassium, yield proximate products of oxidation closely related to the radicals contained in them. Special applications of this process are given on pages 81, 92, &c.

Shortly, the process consists in heating a known weight of the substance in a sealed tube for some hours with an aqueous solution of bichromate of potassium, containing from 3 to 8 per cent. of the salt, and 5 parts by weight of concentrated sulphuric acid to every 4 of the bichromate. The following reactions were verified by the authors of the method as occurring with very considerable accuracy:—



Compounds containing methyl yield formic acid by oxidation, but the greater part of this is further oxidised to carbonic acid and water. Messrs Chapman and Smith†

\* *Journ. Chem. Soc.* xix. 477.

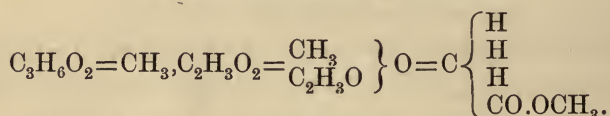
† *Ibid.* xx. 173.

further showed that the process was capable of being used for investigating the structure of isomeric bodies. This is exemplified in the equation representing the oxidation of isopropyl iodide.

The foregoing methods of examining ethers are of such general application, that, with the aid of the leading special properties given on page 140, most of the ethers in common use may be readily identified, and even quantitatively determined. A few, however, owing to their special properties or great individual importance, require separate sub-sections for their consideration.

### **Methyl Acetate.**

*German*—Essigsaurer Holzäther.



This ether closely resembles ethyl acetate, but boils at 56.3° C., and has a density of .919 at 21° C. It is remarkable for being readily soluble in water. It is prepared by processes similar to those employed for obtaining ethyl acetate. It is sometimes present to a considerable extent in crude wood-naphtha. See page 67.

**Acid Methyl Salicylate;** Oil of Winter-green.  $\text{C}_8\text{H}_8\text{O}_3 = \left. \begin{array}{c} (\text{C}_7\text{H}_4\text{O})'' \\ \text{H}(\text{CH}_3) \end{array} \right\} \text{O}_2$ .—This ether exists ready formed in *Gaultheria procumbens* and some other plants, and may be obtained therefrom by distillation with water.

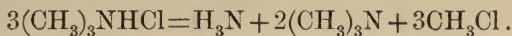
Oil of winter-green may also be prepared artificially by distilling salicylic acid or a salicylate with wood-spirit and strong sulphuric acid.

Natural oil of winter-green contains about 90 per cent. of methyl salicylate, and 10 per cent. of a hydrocarbon isomeric with turpentine. The latter may be separated by fractional distillation, as it boils at 200° C., the methyl salicylate boiling at the temperature of 222° C.

Methyl salicylate is a colourless oily liquid, of penetrating agreeable odour, and sweet, cooling, aromatic taste. Its density at 10° C. is 1.18. It is slightly soluble in water, and is miscible in all proportions with alcohol and ether. The aqueous solution gives a violet colour with ferric chloride. When boiled with aqueous alkalies, oil of winter-green yields pure methyl alcohol and a salicylate.

Methyl salicylate is liable to adulteration with oil of sassafras and with chloroform. The former sophistication may be detected by adding 3 or 4 drops of nitric acid (of 1.3 to 1.4 sp. gr.) to 4 or 5 drops of the oil. Sassafras oil becomes blood-red in colour, and soon changes to a brown amorphous mass. Pure oil of winter-green is unchanged at first, but after some hours it solidifies to a mass of colourless crystals, consisting of methyl-nitro-salicylic acid. Chloroform may be detected by the smell when the sample is warmed. Samples containing chloroform have a high density and low boiling point. The chloroform may be approximately separated and determined by fractional distillation, or by estimating the hydrochloric acid formed on passing the vapour mixed with hydrogen through a red-hot tube.

**Methyl Chloride.** Chlor-methane.  $\text{CH}_3\text{Cl}$ .—This ether is obtained by the co-distillation of methyl alcohol, common salt, and sulphuric acid; also by heating the hydrochlorate of trimethylamine to about 260°, when it suffers decomposition into ammonia, trimethylamine, and methyl chloride.



Methyl chloride is a gas at ordinary temperatures, but is condensed by a pressure of 4.1 atmospheres at 15° C. or 2.5 at 0° C. to a colourless, very mobile liquid, boiling under the ordinary atmospheric pressure at -23° C.

Gaseous methyl chloride has an ethereal smell and a sweet taste. It burns with a green-edged luminous flame. Water

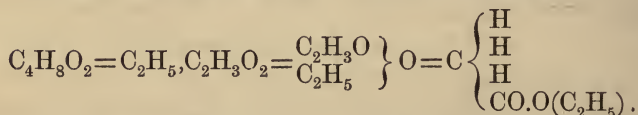


dissolves 3 volumes and alcohol 35 volumes of gaseous methyl chloride. Chloride of methyl is well suited for use as a refrigerating agent, and is employed in the manufacture of methylated aniline dyes.

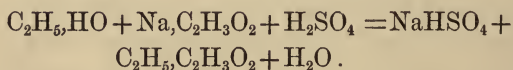
By the continued action of chlorine, methyl chloride yields successively chlorinated methyl chloride, chloroform, and tetrachloride of carbon. Chlorinated methyl chloride and its isomer methylene dichloride are described on p. 182, and chloroform on p. 173, *et seq.*

**Ethyl Acetate.** Acetic ether.

*French*—Ether acétique. *German*—Essigäther.



Acetate of ethyl is generally prepared by distilling sodium or lead acetate with alcohol and sulphuric acid,



Another, but little known, plan is to pass carbon dioxide gas into an alcoholic solution of potassium acetate, when potassium carbonate is precipitated and acetic ether formed.

Acetic ether is a colourless liquid, of very fragrant agreeable odour. It is soluble in 11 or 12 parts of cold water, and is miscible in all proportions with ether and alcohol. When pure it has a density of .8981 at 15.0° C., and .9146 at 0° C. The acetic ether of the British Pharmacopœia has a density of .910, and a boiling point of 74.3° C. Such a product usually contains much free acetic acid, to remove which the liquid should be shaken with potassium carbonate and redistilled. Pure acetic ether boils at 74° C.

The proportion of real ethyl acetate contained in a sample of acetic ether may be ascertained by the general process with alcoholic soda, described on page 140. Any free

acid must be exactly neutralised previously, or its presence taken into account in making the calculation.

The proportion of free acetic acid in ethyl acetate may be ascertained by dissolving the sample in proof spirit and titrating the solution with standard alkali and litmus. Each c.c. of decinormal alkali used represents 6 milligrammes of free acetic acid. Pure acetic ether is perfectly neutral to litmus.

The proportion of alcohol contained in a sample of acetic ether may be roughly estimated by agitating the sample in a graduated tube, with an equal measure of a saturated aqueous solution of calcium chloride. On standing, the real acetic ether rises to the surface, and may be measured off in c.c., the number of which multiplied by .898 gives the grammes of ethyl acetate in the sample taken. The difference between this and the total weight may be regarded as alcohol (and water).

Acetate of ethyl combines with solid calcium chloride, but the compound is decomposed on addition of water.

Ethyl acetate occurs in many wines and in wine-vinegar. It is produced spontaneously in several pharmaceutical preparations,—notably in the tincture of ferric acetate. It possesses considerable solvent powers.

**Ethyl Butyrate.** Butyric ether.  $C_6H_{12}O_2 = C_2H_5, C_4H_7O_2$   
 $= \left. \begin{matrix} C_2H_5 \\ C_4H_7O \end{matrix} \right\} O$ .—Prepared by heating together strong sulphuric acid, butyric acid or a butyrate, and strong alcohol. It has a very fragrant odour, resembling that of pine-apple, in the preparation of the essence of which it is used. Pine-apple rum owes its flavour to the formation of traces of this ether by keeping, from the reaction of the free butyric acid present on the alcohol of the spirit.

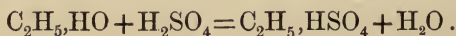
Rum essence consists in great part of ethyl butyrate, and is made by saponifying butter, precipitating the soap by strong brine, and distilling it with sulphuric acid and alcohol.

The product also contains ethylic ethers of the higher homologues of butyric acid.

**Ethyl Pelargonate.** Grape oil. (Ænanthic ether).  
 $C_{11}H_{22}O_2 = C_2H_5, C_9H_{17}O_2 = \left. \begin{matrix} C_2H_5 \\ C_9H_{17}O \end{matrix} \right\} O$ . — Obtained from wine lees, by adding sulphuric acid and water, and distilling in a current of steam. A colourless mobile liquid of powerfully vinous odour. A drop or two added to a quart of spirit of wine, gives it an odour identical with that of cognac. The ether is almost insoluble in water, but readily soluble in alcohol even when dilute. Pelargonic acid may also be obtained from the essential oil of garden rue, and the ether prepared by passing hydrochloric acid gas through the alcoholic solution of the acid. A solid substance is sometimes sold under the name of ænanthic ether, which is used for flavouring inferior and fictitious wines.

**Ethyl - Sulphates.** Sulphovinates.  $M', C_2H_5SO_4 = \left. \begin{matrix} C_2H_5 \\ M' \end{matrix} \right\} SO_4$ .—The sulphovinates are the salts of ethylsulphuric acid, which has the composition of an acid sulphate of ethyl, but possesses decided acid properties, and forms a well-defined series of salts. Hence it might with propriety be considered among the *acid* derivatives of the alcohols.

Ethyl-sulphuric acid is produced by the reaction of alcohol on strong sulphuric acid.



The change is much facilitated by keeping the liquid at a temperature of 100° C. for 24 hours. The less water there is present, the more perfect is the change; but the reaction is always far from complete. If the temperature be raised much above 100° C., ordinary ether is produced, and, at higher temperatures still, ethylene and other products are formed.

From the crude ethyl-sulphuric acid, obtained as above, the salts may be prepared in the following manner:—

BARIUM ETHYL-SULPHATE, by neutralising the product with carbonate of barium, filtering off the insoluble barium sulphate and evaporating the filtrate to crystallisation. The calcium salt may be obtained in similar manner, and the lead salt by employing litharge instead of barium carbonate.

SODIUM ETHYL-SULPHATE,  $\text{NaC}_2\text{H}_5\text{SO}_4 + \text{H}_2\text{O}$ , may be obtained by decomposing one of the above salts with sodium carbonate, or by adding powdered carbonate of sodium and alcohol, or alcoholic solution of caustic soda, to the crude acid, filtering from the insoluble sodium sulphate, and evaporating the filtrate to crystallisation.

Sodium ethyl-sulphate (sulphovinate of sodium), is a white crystalline salt of faint ethereal odour, and cooling, sweetish, somewhat aromatic taste, very deliquescent, soluble in 0·7 parts of cold water, and also soluble in alcohol, with which it is capable of forming a crystalline compound. Sodium ethyl-sulphate is insoluble in ether. It has been employed in medicine as a saline purgative. At  $86^\circ \text{C}$ . sodium, ethyl-sulphate melts and becomes anhydrous; at  $120^\circ \text{C}$ . it decomposes, evolving alcohol vapour, and leaving acid sulphate of sodium. It also decomposes spontaneously at ordinary temperatures, especially when in solution, with formation of sodium sulphate. The presence of a little free alkali prevents this change. The commercial salt is liable to contain barium, calcium, lead, arsenic, sulphates, &c. It is not unfrequently contaminated with foreign organic matter. When pure it does not char on ignition. It has been adulterated by admixture with sulphate of sodium, and has been replaced by acetate of barium. The last dangerous substitution would at once be detected by adding dilute sulphuric acid to the aqueous solution.

The characters of the ethyl-sulphates are sufficiently indicated by the above description of the sodium salt. They are all soluble in water. When heated with dilute sulphuric acid they evolve alcohol, and with strong sul-



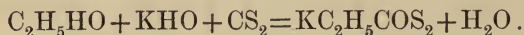
phuric acid, ether. With sulphuric acid and an acetate they give a fragrant odour of acetic ether. The same result is obtained by simply heating together an acetate and sulphovinate.

- ETHYL-SULPHURIC ACID,  $\text{H}_2\text{C}_2\text{H}_5\text{SO}_4$ , may be obtained in a state of purity by decomposing the barium salt by an equivalent amount of dilute sulphuric acid, or a solution of ethylsulphate of lead by sulphuretted hydrogen. On concentrating the filtered liquid, sulphovinic acid is obtained as a limpid, oily, very sour, unstable liquid of 1.31 sp. gr. It is miscible with water and alcohol in all proportions, but is insoluble in ether.

**Ethyl Disulpho-Carbonates; Xanthates.**  $\text{M}'\text{C}_2\text{H}_5\text{S}_2\text{O} = \left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{CO}'' \\ \text{M}' \end{matrix} \right\} \text{S}_2$ .—The xanthates are the salts of xanthic acid,

which, though having the composition of an ether, possesses decided acid properties. Hence, it ought strictly to be considered among the *acid* derivatives of the alcohols.

When boiling absolute alcohol is saturated with pure caustic potash, and carbon disulphide added gradually till it ceases to be dissolved, or the liquid becomes neutral, potassium xanthate is formed, according to the following equation:—



On cooling, the xanthate of potassium crystallises in slender colourless prisms, which must be pressed between blotting paper and dried in a vacuum. Potassium xanthate is readily soluble in water and alcohol, but insoluble in ether. On exposure to air it suffers gradual decomposition.

On adding dilute sulphuric or hydrochloric acid to potassium xanthate, xanthic acid,  $\text{HC}_2\text{H}_5\text{S}_2\text{O}$ , is liberated as a colourless, heavy, oily liquid, of peculiar and powerful odour and astringent bitter taste. It is very combustible. Xanthic acid reddens litmus, and ultimately bleaches it. At a very slight rise of temperature it undergoes decomposition

into alcohol and carbon disulphide. Owing to this property the xanthates have been successfully used as a remedy for the *phylloxera*, which attacks the vine, and is equally efficacious against the ravages of other noxious insects. The xanthate is mixed with earth, either alone or together with superphosphate, when it gradually undergoes decomposition with formation of carbon disulphide.

Xanthic acid possesses powerful antiseptic properties.

When warmed with nitric acid, xanthic acid and xanthates evolve an odour of ethyl nitrite.

On distillation, the xanthates are decomposed with formation of  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{H}_2\text{S}$ , and a peculiar sulphuretted oil, while a metallic sulphide and carbon remain behind.

The most characteristic reaction of xanthic acid, and the one from which it derived its name, is that produced with salts of copper. On adding cupric sulphate to a neutral solution of a xanthate a brownish precipitate of cupric xanthate is first formed, which quickly changes to bright yellow flocks of cuprous xanthate. This substance is insoluble in water and in dilute acids, but is decomposed by strong acids. It is not sensibly attacked by sulphuretted hydrogen, but is instantly decomposed by a soluble sulphide. The formation of cuprous xanthate has been employed for detecting carbon disulphide in coal-gas, the gas being passed through alcoholic potash, the excess of alkali neutralised by carbonic or tartaric acid, the insoluble salt removed by filtration, and the liquid treated with sulphate of copper.

The formation of cuprous xanthate has also been proposed by E. A. Grete as a means of determining copper and caustic alkali.\*

**Ethyl Nitrite.** Nitrous ether.  $\text{C}_2\text{H}_5\text{NO}_2 = \left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{NO} \end{matrix} \right\} \text{O}.$ —

This substance has been known in an impure state for a long time. It may be obtained by passing the red vapours of

\* *Journ. Chem. Soc.* 1876, ii. 551, and *Deut. Chem. Ges. Ber.* ix. 921.

nitrogen trioxide (evolved by acting on starch by nitric acid) into alcohol, by distilling nitrite of potassium or sodium with alcohol and sulphuric acid, or by the direct action of nitric acid on alcohol. In the last case the nitric acid is reduced by a portion of the alcohol, and the nitrous acid so formed acts on the remainder to form ethyl nitrite. A considerable quantity of aldehyde results from the oxidation of the alcohol, so that the ether obtained by this process is largely contaminated. In the official process of the British Pharmacopœia, the formation of much aldehyde is avoided by the addition of metallic copper, but traces are always produced.

Pure nitrite of ethyl is a nearly colourless liquid, of very fragrant odour. It is soluble in all proportions in alcohol, but requires forty-eight parts of water for solution. It boils at  $18^{\circ}\text{C}$ ., and has a density of  $\cdot 947$  at  $15\cdot 5^{\circ}\text{C}$ . ( $60^{\circ}\text{F}$ .). It is liable to decompose on keeping, especially in presence of water. It gives many of the ordinary reactions of the nitrites. Thus, when mixed with a little dilute sulphuric acid, and poured on a strong aqueous solution of ferrous sulphate, it develops a dark-brown colour. When dissolved in alcohol, and treated with a few drops of dilute sulphuric or acetic acid, it liberates iodine from potassium iodide, and therefore the mixture produces the well-known blue colour on addition of starch.

Nitrite of ethyl is rarely met with in a pure state, but its solution in rectified spirit constitutes the Pharmacopœia preparation known as

SPIRIT OF NITROUS ETHER (*Spiritus ætheris nitroci*, B. P.)—This is a preparation corresponding to the sweet spirit of nitre of commerce, both articles having a similar composition. The characters of “spirit of nitrous ether” are thus described in the British Pharmacopœia:—

“Transparent and nearly colourless, with a very slight tinge of yellow, mobile, inflammable, of a peculiar penetrating apple-like odour, and sweetish, cooling, sharp taste. Specific gravity,  $0\cdot 845$ . It effervesces feebly, or not at all, when

shaken with a little bicarbonate of soda. When agitated with solution of sulphate of iron and a few drops of sulphuric acid, it becomes a deep olive-brown or black. If it be agitated with twice its volume of saturated solution of chloride of calcium in a closed tube, 2 per cent. of its original volume will separate in the form of nitrous ether, and rise to the surface of the mixture."

The presence of aldehyde in sweet spirit of nitre is indicated by the production of a brown colour on heating the sample with caustic potash.

Spirit of nitrous ether has often a great tendency to become acid. This may be due to the decomposition of the nitrous ether, or, in presence of air, to the oxidation of the aldehyde with formation of acetic acid.

Much of the spirit of nitrous ether of commerce is made *originally* of '850 specific gravity, but it is often largely diluted with water, a common practice being the addition of one volume of water to every three of the spirit. An inferior spirit, of specific gravity '900, is sold wholesale.

The proportion of water present in spirit of nitrous ether can be determined with all desirable accuracy by taking the specific gravity of the sample (for details, see page 82). The Pharmacopœia article, having a density of '845, contains, according to the alcohol table on page 85, 81·7 per cent. by weight of absolute alcohol, or 152·4 per cent. by volume of proof spirit. The density of the sample being taken, and the corresponding percentage of proof spirit found by reference to the table, the extent to which the sample has been diluted with water is obtained by dividing the percentage of proof spirit found in the sample by 1·524, which gives the percentage by volume of spirit of nitrous ether of British Pharmacopœia strength which is contained in the sample.

The density of the sample merely indicates the proportion of water, the nitrous ether being present in too small a proportion sensibly to affect the specific gravity.

The addition of water to sweet spirit of nitre is a highly



objectionable practice, for it not only reduces the immediate strength and medicinal value of the preparation, but also renders it far more liable to change, owing to the tendency of ethyl nitrite to decompose in presence of water. In fact, much of the sweet spirit of nitre of commerce contains *little or no nitrous ether*. This is sometimes due to preparation with too weak an alcohol, but is more frequently consequent upon adulteration of the manufactured article by addition of water. The author found that a sample of spirit of nitrous ether kept perfectly well for very many months when undiluted, but the same sample when mixed with one-third of its measure of water contained no nitrous ether after an interval of four months.

Mr J. Williams has observed the same fact, and has proposed to substitute for the present indefinite preparation a solution of pure ethyl nitrite in nine or nineteen times its weight of absolute alcohol. Such a preparation appears to be thoroughly permanent, and if rectified spirit be substituted for the absolute alcohol the solution is still very stable.

A useful test for detecting and roughly judging the amount of nitrous ether in the commercial spirit is that with ferrous sulphate. A saturated aqueous solution of ferrous sulphate should be prepared, and mixed with an equal measure of pure concentrated sulphuric acid. When the mixture is quite cold, 5 c.c. are poured into a test-tube, and an equal volume of the sample of spirit poured on the top of it in such a manner as to avoid admixture of the two liquids. A deep-brown ring will be formed at the junction of the two layers, if nitrous ether be present. By gently agitating the liquid, the colour usually becomes stronger, and, with a little experience, the depth of tint on complete admixture will give the observer a fair indication of the amount of nitrous ether present.

The B. P. test, by treating the sample with two volumes of a saturated solution of calcium chloride, is best performed in a narrow graduated tube, which the mixture should nearly fill.

The spirit should be poured into the tube first, and cooled, the chloride of calcium solution next added, and then a tightly-fitting cork immediately inserted, and tightly pressed in by the thumb while the tube is shaken to mix the contents. As the tube will now be under considerable pressure, it is convenient to reverse the tube and fix it tightly in the clamp of a burette-stand, the cork being kept thus tightly pressed against the foot. Half-an-hour should be allowed for the nitrous ether to rise to the closed end of the tube, and its volume is then read off. The process is very unsatisfactory, for less than 8 per cent. of ether gives no indication, and it by no means follows that any that is indicated is really nitrous ether. When no separation of ethereal liquid takes place, 100 c.c. of the sample should be treated with dry chloride of calcium, and 20 c.c. distilled off at a gentle heat. An aliquot part of the distillate may then be treated by the Pharmacopœia test, and the proportion of ether indicated calculated to the whole amount. Thus, if 10 c.c. of the distillate be shaken with saturated chloride of calcium solution, and 1 c.c. of ether be thus separated, then, with the .8 c.c. (8 per cent. of 10 c.c.) which remains dissolved, this will make 1.8 c.c. from 100 c.c. of the sample, or 1.8 per cent.

The accurate determination of the real ethyl nitrite existing in commercial samples of spirit of nitrous ether is not very readily effected. The general process for the analysis of compound ethers given on page 140 does not give accurate results, owing to the presence of aldehyde, which reacts on the standard alkali used. By treatment with an oxidising agent, the nitrite may be wholly converted into nitric acid, but the determination of the latter is not very simply effected. Nor has the author obtained good results by a process suggested by Dupré, which is based on decomposition of the ether by alkali and titration of the resultant nitrite by standard permanganate.

The preparation of spirit of nitrous ether from methy-

lated spirit is illegal, but is occasionally practised. The detection of the fraud may be effected by the following process, devised by Mr J. T. Miller. The description is taken from Attfield's "Chemistry":—

"Shake about an ounce of the sample with twenty or thirty grains of anhydrous carbonate of potassium, and, if needful, add fresh portions of the salt until it ceases to be dissolved, then pour off the supernatant spirit. This serves to neutralise acid and to remove water, in which some samples are remarkably rich. Introduce half a fluid ounce of the spirit into a small flask, add 150 grains of anhydrous chloride of calcium in powder, and stir well together; then, having connected the flask with a condenser, place it in a bath of boiling water, and distil a fluid drachm and a half, or continue the distillation until scarcely any more comes over. The operation is rather slow, but needs little attention, and should be done thoroughly. The distillate contains nearly the whole of the nitrous ether and other interfering substances. Now add to the contents of the flask a fluid drachm of water, and draw over the half drachm of spirit required for testing. Add to it the usual oxidising solution, composed of thirty grains of red chromate of potassium, twenty-five minims of strong sulphuric acid, and half an ounce of water; let the mixture stand a quarter of an hour, then distil half a fluid ounce. Treat the distillate with a slight excess of carbonate of sodium, boil rapidly down to two fluid drachms, and drop in cautiously enough acetic acid to impart a faint acid reaction; pour the liquor into a test-tube about three-quarters of an inch in diameter, add two drops of *diluted* acetic acid (B. P.) and one grain of nitrate of silver in half a drachm of pure water; apply heat, and boil gently for two minutes. If the spirit is free from methylic alcohol the solution darkens, and often assumes transiently a purplish tinge, but continues quite translucent, and the test-tube, after being rinsed out and filled with water, appears clean, or nearly so. But if the spirit contains only 1 per cent.

of methylic alcohol, the liquid turns first brown, then almost black and opaque, and a film of silver, which is brown by transmitted light, is deposited on the tube. When the sample is methylated to the extent of 3 or 4 per cent., the film is sufficiently thick to form a brilliant mirror. To ensure accuracy, the experiments should be performed by daylight."

**Ethyl Chloride.** Hydrochloric ether. "Sweet spirit of salt."  $C_2H_5Cl$ .—Ethylic chloride is a fragrant, exceedingly volatile liquid of 1·370 sp. gr., at  $0^\circ C$ . It boils at  $11^\circ C$ . ( $=50^\circ F$ ). It is sparingly soluble in water, but readily so in alcohol. Its solution in an equal volume of the latter liquid is sometimes employed in medicine. The ether is prepared by distilling alcohol, sulphuric acid, and common salt together, or by passing dry hydrochloric acid gas into absolute alcohol; by adding chloride of zinc to the alcohol, the whole of the latter may be converted into ethyl chloride.

By the continued action of chlorine on ethyl chloride a series of substitution products are obtained, as follow:—

	Boiling Point.	Specific Gravity.
	$^\circ C$ .	
$C_2H_5Cl$ . Ethyl chloride, or chlor-ethane	11	·921 at $0^\circ$
$C_2H_4Cl_2$ . Ethylidene chloride, chlorinated ethyl chloride, or dichlor-ethane	60–64	1·174 at $17^\circ$
$C_2H_3Cl_3$ . Dichlorinated ethyl chloride, or trichlor-ethane	75	1·372 at $0^\circ$
$C_2H_2Cl_4$ . Trichlorinated ethyl chloride, or tetrachlor-ethane	102	1·530 at $17^\circ$
$C_2HCl_5$ . Tetrachlorinated ethyl chloride, or pentachlor-ethane	146	1·644
$C_2Cl_6$ . Carbon trichloride	182	2·0

The last product is a crystalline substance, identical with that produced by the action of chlorine on Dutch liquid. The dichlor-ethane of the above series is only isomeric, and not identical, with ethylene dichloride or Dutch liquid.

The above bodies are produced sometimes on a considerable scale in the manufacture of chloral (see note, page 164). A



very variable mixture of the middle members of the series is at present an article of commerce under the name of *Liquor anæstheticus*. Another similar mixture, containing the less chlorinated bodies, is the *Æther anæstheticus Aranii*, boiling between  $64^{\circ}$  and  $100^{\circ}$  C. The *Æther anæstheticus Wiggers* contains the more highly chlorinated products, and boils between  $100^{\circ}$  and  $140^{\circ}$  C.

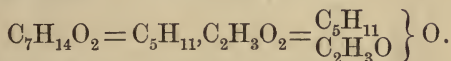
ETHYLIDENE CHLORIDE, CHLORINATED ETHYL CHLORIDE, or DICHLOR-ETHANE,  $C_2H_4Cl_2 = CH_3 \cdot CHCl_2$ , is now prepared in a pure state by the action of chlorine on ethyl chloride, or by distilling aldehyde with phosphorus pentachloride. The boiling point and specific gravity are given above. Ethylidene chloride possesses valuable properties; for while it produces anæsthesia in dogs and rabbits in three or four minutes, there is no sign of failure of the heart's action. In this respect it differs from chloroform and methylene dichloride, both of which deteriorate the action of the heart. The isomer of chlorinated ethyl chloride, the dichloride of ethylene or Dutch liquid,  $(C_2H_4)Cl_2$ , boils at  $84.9^{\circ}$  C., has a density of 1.256 at  $12^{\circ}$  C., and produces severe convulsions when its vapour is inhaled. Ethylidene chloride is distinguished from Dutch liquid by its negative reaction with potassium, whereas the latter is violently acted on by potassium, forming a porous mass and evolving hydrogen and chlor-ethylene,  $C_2H_3Cl$ , the latter being a gas of alliaceous odour. The same gas is produced when Dutch liquid is heated with alcoholic potash, while ethylidene chloride is unaffected by the same reagent. The boiling point and density also distinguish Dutch liquid from its isomer. From chloroform, ethylidene chloride is distinguished by its density, boiling point, and negative reaction with Hofmann's test (see page 174).

**Ethyl Bromide.** Hydrobromic ether. Brom-ethane.  $C_2H_5Br$ .—This ether has recently been employed in medicine as a substitute, in certain cases, for chloroform. It boils at  $40.7^{\circ}$  C., and has a density of 1.40. It burns with difficulty,

giving a bright green, but smokeless, flame, and forming fumes of hydrobromic acid. The boiling point and the smokeless flame distinguish it from ethyl chloride.

**Ethyl Iodide.** Hydriodic ether.  $C_2H_5I$ .—This ether derives its chief interest from its employment in organic research, but it has lately been prepared on a large scale for the preparation of the aniline colours known as “iodine green” and “Hofmann’s violet.” Ethyl iodide is prepared by the action of iodine and phosphorus on alcohol. It is a volatile liquid, colourless when pure, but gradually turning brown in the light. It has a density of 1.946 at  $16^\circ C$ ., and boils at  $72^\circ C$ . It is but slightly soluble in water, but readily so in alcohol and ether.

**Amyl Acetate.** Acetate of pentyl.



—Obtained by distilling amyl alcohol with an acetate and sulphuric acid. When pure, it is a colourless liquid having an exceedingly fragrant odour. It is insoluble in water, but soluble in all proportions in ether, amyl alcohol, and ordinary alcohol. The last solution constitutes the essence of jargonelle pear of commerce. Amyl acetate boils at  $140^\circ C$ ., and has a density of .8763 at  $15^\circ C$ .

It may be determined by the general method on page 140. From alcohol it may be separated by agitating the liquid with an equal measure of saturated solution of chloride of calcium, which dissolves the alcohol only.

Any admixture of amyl alcohol may be separated and determined approximately by treating the sample in a graduated tube with a mixture of equal volumes of glacial acetic acid and water. This dissolves amyl alcohol, but leaves the amyl acetate insoluble (together with any valerate or pelargonate of amyl which may be present). By first separating the ethyl alcohol by salt water, or petroleum spirit, as

described on page 119, this method may be applied to the essence of jargonelle pear.

**Amyl Nitrite.**  $C_5H_{11}NO_2 = \left( \begin{smallmatrix} C_5H_{11} \\ NO \end{smallmatrix} \right) \} O$ .—Prepared by processes similar to those employed for obtaining nitrite of ethyl, amyl alcohol being substituted for spirits of wine. To obtain a product fit for medicinal use, the amyl alcohol should be carefully purified, and have a boiling point of  $129^\circ$  to  $132^\circ$  C. By passing nitrous acid gas into this alcohol, a very pure nitrite is obtained. After washing the product with water and solution of carbonate of sodium, the oily liquid is rectified, the fraction passing over between  $90^\circ$  and  $100^\circ$  C. being retained. On redistillation, amyl nitrite suffers partial decomposition, a neutral liquid furnishing a decidedly acid distillate, and the last portions boiling above  $100^\circ$  C.

Amyl nitrite is a yellowish liquid which boils at  $95^\circ$  to  $100^\circ$  C., giving an orange-coloured vapour having a very powerful effect on the system when inhaled. The density is  $\cdot 877$ , but this indication is of little value, as very impure samples often have a gravity differing very little from the above.

When submitted to fractional distillation, at least 80 per cent. of a good sample of amyl nitrite will pass over between  $90^\circ$  and  $100^\circ$  C.

Amyl nitrite is insoluble in water, but soluble in alcohol in all proportions. It may be estimated by the same methods as ethyl nitrite.

A characteristic test for nitrite of amyl is the formation of valerate of potassium, when the liquid is dropped on fused caustic potash.

Concentrated sulphuric acid attacks nitrite of amyl with great energy, with evolution of red fumes, and formation of a black, foul-smelling liquid. Occasionally the mixture catches fire.

**Artificial Fruit Essences.**—The natural bouquets and flavours of fruits have been found in many instances to depend

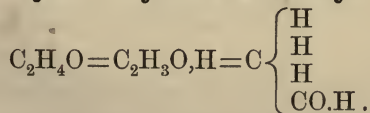
on the presence of small quantities of certain ethers, and they are now prepared on a very extensive scale by the admixture of the artificially produced ethers in suitable proportions.

The following table, taken from Vincent's "Manufacturing Chemistry," shows the composition of various artificial fruit essences and flavours. The numbers given indicate the number of measures of the ethers, &c., to be added to each 100 measures of alcohol of '830 specific gravity. The chloroform and aldehyde can be omitted in most cases without serious detriment to the flavour. In cases in which acids are employed, the figures refer to volumes of a cold saturated solution of the acid in alcohol of '830 specific gravity:—

	Pine-apple.	Melon.	Strawberry.	Raspberry.	Currant.	Grape.	Apple.	Pear.	Cherry.	Plum.	Apricot.	Peach.
Chloroform . . .	1	...	...	...	...	2	1	...	...	...	1	...
Aldehyde . . .	1	2	...	1	1	2	2	...	...	5	...	2
Methyl salicylate . . .	...	...	1	1	...	1	...	...	...	...	...	...
Ethyl nitrate . . .	...	...	1	1	...	...	1	...	...	...	...	...
" formate . . .	...	1	1	1	...	2	...	...	...	1	...	5
" acetate . . .	...	...	5	5	5	...	1	5	5	5	...	5
" butyrate . . .	5	4	5	1	...	...	...	...	...	2	10	5
" valerate . . .	...	5	...	...	...	...	...	...	...	...	5	5
" pelargonate . . .	...	...	...	1	1	10	...	...	...	...	...	...
" benzoate . . .	...	...	...	1	1	...	...	...	5	...	...	...
" sebate . . .	...	10	...	1	...	...	...	...	...	...	...	1
Amyl alcohol . . .	...	...	...	...	...	...	...	...	...	...	2	2
" acetate . . .	...	...	3	1	...	...	...	10	...	...	...	...
" butyrate . . .	10	...	2	1	...	...	...	...	...	...	1	...
" valerate . . .	...	...	...	...	...	...	10	...	...	...	...	...
Tartaric acid . . .	...	...	...	1	5	5	...	...	...	...	...	...
Oxalic acid . . .	...	...	...	...	...	...	1	...	...	...	...	...
Succinic acid . . .	...	...	...	1	1	3	...	...	...	...	...	...
Benzoic acid . . .	...	...	...	...	1	...	...	1	1	...	...	...
Glycerin . . .	3	3	2	4	...	10	4	10	3	8	4	5
Peach oil (ben- zoic aldehyde) }	...	...	...	...	...	...	...	...	1	4	1	5

## ALDEHYDE.

**Acetic Aldehyde. Hydride of Acetyl.**



Ordinary aldehyde is the type of a large series of bodies



which occupy an intermediate position between the alcohol radicals and their corresponding acids. Although the term aldehyde is now employed generically, when used as a proper name it is always understood to mean acetic aldehyde.

Aldehyde results from the destructive distillation of various organic compounds, and from the limited oxidation of alcohol by dilute chromic acid, nitric acid, air in presence of platinum black, &c.

In practice, aldehyde is prepared by distilling together alcohol, sulphuric acid, and manganese dioxide, but it may be obtained in various other ways.

Aldehyde is a mobile, colourless liquid, having a pungent suffocating odour. In pure samples, the disagreeable odour is much less marked than in the crude substance. Its density is  $\cdot 790$ , and it boils at  $22^{\circ}$  C. It does not redden litmus, either when absolute or when in solution. It turns acid on exposure to air, from oxidation to acetic acid.

Aldehyde is miscible in all proportions with water, alcohol, and ether. It is not soluble in a saturated solution of calcium chloride. This fact is not of service for the quantitative separation of aldehyde from alcohol. A better method of separation is to treat the liquid with dry calcium chloride, which forms a compound with the alcohol, when the aldehyde may be distilled off by the heat of a water-bath.

Aldehyde is very inflammable, and burns, when kindled, with a blue flame. Aldehyde when exposed to the air suffers rapid conversion into acetic acid. When kept in closed vessels it often becomes converted into liquid or solid modifications. The alcoholic solution of aldehyde is tolerably permanent. Oxidising agents convert aldehyde into acetic acid. Dehydrating agents, such as phosphoric anhydride and concentrated sulphuric acid, when heated with aldehyde turn it thick and black. Aldehyde may be distilled from sulphuric acid diluted with an equal weight of water.

In aqueous or alcoholic solution, aldehyde is best recognised

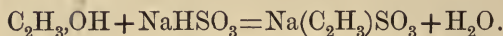
by its reaction when heated with caustic alkali. When thus treated, the liquid becomes yellow and turbid, and a reddish-brown resinous mass rises to the surface, the liquid emitting a highly disagreeable odour. The solution contains a formate and acetate of alkali-metal. This formation of the aldehyde-resin is the most characteristic reaction of aldehyde, and has been utilised by J. C. Thresh\* for its approximate determination. To effect this, 1 part of pure aldehyde should be diluted with 200 measures of water, 30 measures of a syrupy solution of caustic soda added, and the whole heated and kept at the boiling point for a few seconds. It is then allowed to cool, and after standing two hours is diluted with 200 measures of warm methylated spirit (free from aldehyde), and then made up to 500 measures by addition of water. This solution is quite clear, and of a reddish-yellow colour. As it quickly alters, it is desirable to make a solution of bichromate of potassium of the same tint, and employ that instead of the original liquid. To determine aldehyde, the liquid containing it, suitably diluted and previously distilled if necessary, is treated in exactly the same manner as the pure aldehyde, and the colour of the liquid obtained compared with the standard, and the darker diluted with water till the tints are identical. The comparison is effected in much the same manner as in Nessler's method of determining ammonia.

Aldehyde is a powerful reducing agent. It separates metallic silver from the ammonio-nitrate, often in a specular form, whilst acetate of silver is found in the liquid. Fehling's solution gives a copious precipitate of red cuprous oxide when heated with a solution of aldehyde. Neither of these reactions have, in the hands of the author, proved serviceable for the determination of aldehyde.

A characteristic property of aldehyde, but common to all bodies of the class, is the formation of white crystalline com-

\* *Pharm. Journ.* Nov. 16, 1878, page 409.

pounds with the acid sulphites of the alkali-metals. The formation of these bodies is best explained by regarding aldehyde as vinylic hydrate,  $C_2H_3.OH$ .



These compounds are soluble in alcohol and water, but insoluble in strong solutions of the acid sulphites. Hence, by adding excess of acid sodium sulphite to an aqueous solution of aldehyde, the latter substance may be entirely separated, and can be obtained in a free state by distillation with a dilute mineral acid or an alkaline carbonate.

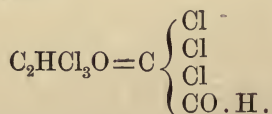
Aldehyde also combines with ammonia, forming a crystalline substance of the formula  $C_2H_4O.NH_3$ , which is insoluble in ether and is decomposed on distillation with moderately dilute sulphuric acid.

ACROLEIN, VALERAL, and the ESSENTIAL OILS of bitter-almonds, cinnamon, cumin, and meadow-sweet consist, wholly or chiefly, of bodies of the aldehyde class. All these form crystalline compounds with the acid sulphites of alkali-metals.

ACETONE (page 70) has the composition of methyl-aldehyde, and chloral is a trichlor-aldehyde.

## CHLORAL.

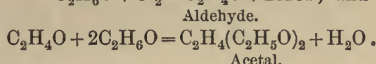
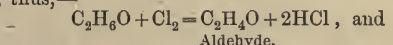
### Trichlor-aldehyde.



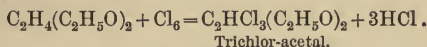
Chloral is obtained in practice by the prolonged action of dry chlorine on absolute alcohol. When the liquid possesses a density of 1.400, it is distilled with an equal weight of strong sulphuric acid, the process being stopped when the temperature rises to  $100^\circ C$ . The distillate is neutralised with chalk and again distilled. The reactions which occur in the manu-

facture of chloral are very complicated, and various secondary products are formed.\*

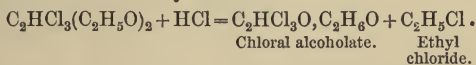
\* The action of chlorine on absolute alcohol results in the formation of aldehyde and acetal, thus,—



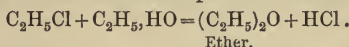
By the continued action of chlorine, that element replaces three atoms of hydrogen,—



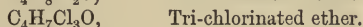
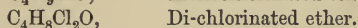
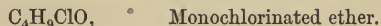
Trichlor-acetal may be regarded as a compound of chloral with ether,  $C_2HCl_3O, (C_2H_5)_2O$ . By reaction with the generated hydrochloric acid this yields chloral alcoholate and ethyl chloride :—



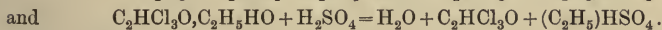
Most of the latter reacts with the alcohol present to form ether,



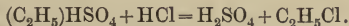
The ether thus formed is converted by fresh chlorine into the following chlorinated products :—



During the subsequent distillation with concentrated sulphuric acid, the tetra-chlorinated ether and the chloral alcoholate split up into chloral and ethyl-sulphuric acid, as follows :—



The ethyl-sulphuric acid reacts with hydrochloric acid to form sulphuric acid and ethyl chloride,



By the continued action of chlorine on tetra-chlorinated ether, a penta-chlorinated ether is produced ( $C_2H_5, O, C_2Cl_5$ ). This body has a density of 1.65, and does not yield chloral when treated with sulphuric acid. Hence, in practice, the current of chlorine gas is interrupted when the liquid has reached a density of 1.40.

By reacting on the ethyl chloride formed in the process, chlorine produces a whole series of chlorinated substitution products (see page 157).

By the chlorination of two associated molecules of aldehyde, a substance called butyl-chloral is formed, having the formula  $C_3H_5Cl_3O$ . It is distinguished from ordinary chloral by its boiling point and the melting point of its hydrate, as well as by the mode of its decomposition by alkalis (see page 171).

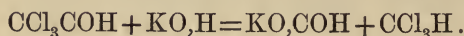
The occurrence of many or all of the above reactions sufficiently accounts for



Anhydrous chloral is a thin oily liquid, of a density of 1.502 at 18° C. It boils at 94° C. It is soluble in ether or chloroform without change.

When kept for some time, or when left in contact with concentrated sulphuric acid, chloral is converted into an insoluble modification called meta-chloral,  $C_6H_3Cl_3O_3$ , which is insoluble in water.

By the action of aqueous alkalies chloral yields chloroform and a formate, thus:



If an aqueous solution of chloral be heated to 50° C. with zinc, and very dilute acid gradually added, aldehyde and para-aldehyde are formed, and may be distilled off.  
 $C_2HCl_3O + H_6 = 3HCl + C_2H_4O.$

When chloral is mixed with an equivalent quantity of absolute alcohol it is converted into

**Chloral Alcoholate**,  $C_4H_7Cl_3O_2 = C_2HCl_3O, C_2H_6O$ .—This substance forms white crystals, which melt at 46° C. It boils at 113.5° C. (See page 167.) These properties, among others, distinguish it from

**Chloral Hydrate**,  $C_2H_3Cl_3O_2 = C_2HCl_3O, H_3O = CCl_3 \cdot CH(OH)_2$ .—This important substance results from the mixture of equivalent quantities of anhydrous chloral and water. The mixture becomes heated and solidifies to a mass of crystals of the hydrate. Chloral hydrate is soluble in  $1\frac{1}{2}$  times its weight of water. It is also soluble in alcohol, ether, and carbon disulphide. When crystallised from the last solution it boils at 97.5° C. Chloral hydrate is soluble with difficulty in cold chloroform, requiring 4 times its weight, a fact which distinguishes it from the alcoholate, which is readily soluble in chloroform.

the variety of the impurities sometimes contained in commercial chloral hydrate and chloroform. The distinction between the different chlorinated oils, and their recognition in chloroform, chloral, &c., can at present be effected but very imperfectly.

In the following table are given other useful distinctions between chloral alcoholate and chloral hydrate:—

	Chloral Alcoholate.	Chloral Hydrate.
1. Melting point.	46° C.	48°–49° C.
2. Boiling point.	113·5° C.	97·5° C.
3. Density of the fused substance at 66° C.	1·344	1·57
4. Sp. gr. of the aqueous solution at 15·5° C.		
5 per cent.	1·007	1·019
10    "	1·028	1·040
15    "	1·050	1·062
20    "	1·071	1·085
5. Gently heated with nitric acid of 1·2 sp. gr.	Violently attacked.	Scarcely acted on.
6. Shaken with an equal volume of strong sulphuric acid.	Brown coloration.*	No visible change.*
7. Warmed with two volumes of water.	Melts without complete solution, and on cooling congeals below the surface.	Readily dissolved.
8. Heated on platinum foil.	Inflames readily.	Scarcely burns.

Chloral hydrate and alcoholate should be completely volatile. Their aqueous solutions should be perfectly neutral to litmus.

An aqueous solution of chloral hydrate gives no reaction with silver nitrate in the cold, but when the liquid is heated to boiling, and a few drops of ammonia added, a metallic mirror is readily produced. If kept some time, chloral hydrate contains a trace of hydrochloric acid, and then gives a cloud with nitrate of silver; the production of a distinct precipitate indicates serious impurity.

When the water of hydration is in excess, chloral hydrate is deliquescent, or even melts in warm weather. Chloral hydrate is now generally made slightly deficient in hydration. If more than a shade short of being fully hydrated the product has a tendency to become acid, and partially insoluble from production of meta-chloral.

\* Other impurities besides the alcoholate cause a darkening with sulphuric acid.

The point of solidification of melted chloral hydrate is an indication of some value. The sample should be placed in a small test-tube, fused, and the tube immersed in water at about 55° C. (131° F.) A thermometer is placed in the chloral, and the temperature at which the liquid becomes opalescent noted. The best chloral hydrate solidifies at about 48° to 49° C., and the best *practically* adjusted specimens within half a degree of 50° C. A low freezing-point indicates excess of water, and such specimens are liable to deliquesce. Small granular crystals and saccharoid masses are purer than large crystals or needles.

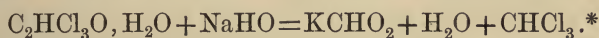
The boiling point of chloral hydrate is also of service as a test of purity. The sample should be placed in a test-tube with some broken glass. With a pure sample, rapid boiling commences at 97° C., and the temperature will not vary very much till fully one-half has been volatilised. Chloral hydrate appears, however, to undergo slow decomposition at its boiling point, so that the first portions of the distillate are under-hydrated, and the last over-hydrated. The boiling point consequently undergoes a gradual rise. The best commercial specimens, those slightly under-hydrated, begin to boil throughout the liquid at about 96·5° C. The under-hydrated portion boils off in a few seconds, and the boiling point rises to 97° C., and finally to 97·5° or 98° C., by the time half the liquid has boiled off. A boiling point above 98° C. indicates an over-hydrated and deliquescent sample. If the boiling fairly commences below 95° C., the sample is too much under-hydrated, and is liable to decompose on keeping (E. R. Squibb).

When mixed with an equal weight of camphor, chloral hydrate rapidly liquefies with a slight rise of temperature. The liquid smells of both its constituents; it does not precipitate nitrate of silver.

Chloral hydrate reduces Fehling's copper solution. The reaction may be employed to detect traces of chloral if other reducing substances be absent, and might probably be employed for the determination of chloral.

Traces of chloral may be detected by Hofmann's delicate test for chloroform (see page 174); also, by boiling the liquid and passing the vapour through a red-hot tube, when hydrochloric acid will be formed, and hence the condensed water will precipitate silver nitrate.

1. For the determination of real chloral in commercial samples of the hydrate, advantage may be taken of its reaction with alkalis, which results in the separation of chloroform and the production of an alkaline formate.



K. Müller treats 25 grammes of the sample in a finely-graduated tube, and then adds a strong solution of caustic potash, in quantity rather more than sufficient for the above reaction. A large excess of alkali must be avoided. The tube must be kept well cooled, as the action is very violent at first. Afterwards, the tube may be closed and the mixture shaken. After resting an hour or two the liquid becomes clear, and separates into two layers. The lower layer is chloroform, and after being brought to a temperature of 17° C., the volume may be read off. Its density is 1.491. Thus the measure of chloroform in cubic centimetres multiplied by 1.840 gives the grammes of anhydrous chloral in the quantity of the sample employed. If the factor 2.064 be substituted, the product will be the weight of chloral hydrate present. Müller obtained by this process an average of 71.6 per cent. of chloroform from pure chloral hydrate, against 72.2 per cent. as required by theory.

2. Ammonia may be substituted for potash or soda in the above process, 10 grammes of the sample being dissolved in as little water as possible, and treated with 5 c.c. of ammonia of 0.90 sp. gr. The tube should be well closed and immersed in warm water (40° C.) for some hours, and plenty of time allowed for the chloroform to separate. The reaction is liable to be incomplete. In one experiment the author obtained

\* TRICHLOR-ACETIC ACID is decomposed in a similar manner, and responds to all the tests for chloral dependent on its conversion into chloroform.



only 70 per cent. from a sample which by other methods yielded 98.0 per cent.

3. C. H. Wood\* objects to the length of time and large quantity of the sample required for the ammonia process, and prefers to decompose the chloral with milk of lime. He takes 100 grains (about 7 grammes) of the sample, dissolves it in an ounce (30 c.c.) of water, and places it in a 4 ounce flask. He then adds 40 grains ( $2\frac{1}{2}$  grammes) of slaked lime. A cork with a tube bent twice at right angles is next adapted to the flask, the outer end of the tube being somewhat drawn out and immersed in a small quantity of water, contained in a narrow graduated glass tube surrounded with cold water. A gentle heat is applied to the flask, and the chloroform slowly distilled over. After a few minutes the heat is gradually increased, so as to keep the mixture boiling, the operation being continued till 100 grain measures (7 c.c.) have passed over. Nothing remains but to bring the chloroform to the proper temperature and read off the volume. The addition of a few drops of potash solution destroys the meniscus of the chloroform, and enables the operator to read off accurately. The process does not occupy more than a quarter of an hour. Too much lime occasions frothing, but an excess appears to have no decomposing action on the chloroform. Lieben's iodoform test for alcoholate is readily applied to the aqueous portion of the distillate. The author has found this plan convenient and fairly accurate. In all the above processes a correction may advantageously be made for the slight solubility of chloroform in aqueous liquids. This is about .3 c.c. for every 100 c.c. of aqueous liquid.

4. A very simple and accurate modification of the above process for assaying chloral hydrate has been suggested by M. Meyer, and has given the author very satisfactory results. It has the advantage of being applicable to very moderate quantities of material. 1 or 2 grammes of the sample are

\* *Pharm. Journ.* 3d series, i. 703.

dissolved in water, and, if any free acid be present, it is removed by shaking the liquid with chalk or barium carbonate, and subsequently filtering. The filtrate is then treated with a moderate excess of standard caustic soda, and titrated back with acid in the usual way, litmus being used as an indicator. Each c.c. of normal alkali neutralised by the sample corresponds to 1.475 grammes of real chloral ( $C_2HCl_3O$ ), or 1.655 grammes of chloral hydrate.

5. Versmann\* has proposed to treat 10 grammes of the sample of chloral hydrate with 5 or 6 c.c. of concentrated sulphuric acid at  $60^\circ C$ . in a graduated tube furnished with a stopper. The mixture is shaken, and the tube put back in the hot water for a few minutes. A layer of anhydrous chloral floats on the acid, and from its volume after cooling, and density (which is 1.502 at  $18^\circ C$ .), the proportion in the sample is readily calculated. The theoretical proportion of real chloral in the pure hydrate is 89.12 per cent., and in the alcoholate 76.23. Versmann got results which agreed with those obtained by ammonia, but the author's experiments were very unsatisfactory, the percentage of chloral found being considerably below the truth. The error is probably due to the formation of compound of chloral with the acid.

**Butyl-Chloral. Butyric Chloral.**—Butyric trichlor-aldehyde. *Erroneously*, Croton chloral.  $C_4H_5Cl_3O = C_3H_4Cl_3.CO.H$ . When chlorine is passed into aldehyde, this substance is formed in addition to ordinary chloral. It bears the same relation to butyl alcohol and butyric acid that ordinary chloral bears to ethyl alcohol and acetic acid.

Butyl-chloral was at first called croton-chloral, the hydrogen being under-estimated, which led to the supposition that it was the trichlorinated aldehyde of crotonic acid,  $C_4H_6O_2$ , the fourth member of the acrylic or oleic acid series.

Butyric chloral is a dense oily liquid of peculiar odour,

\* *Pharm. Journ.* 3d series, i. 701.

boiling at about  $163^{\circ}\text{C}$ . When treated with a considerable excess of warm water it dissolves, and on cooling deposits

**Butyric or Butyl Chloral Hydrate.**  $\text{C}_4\text{H}_5\text{Cl}_3\text{O}\cdot\text{H}_2\text{O}$ .—This substance forms white silvery crystals melting at  $78^{\circ}\text{C}$ ., and having a sweetish melon flavour.

It is but little soluble in cold water, but more so in hot. Its solubility is increased by addition of glycerin. It is very soluble in alcohol, but insoluble, or nearly so, in chloroform. This last property may be employed to separate it approximately from ordinary chloral hydrate. It also differs from the latter body in its melting and boiling point.

When acted on by alkalis, butyric chloral hydrate is at first decomposed with production of propylic chloroform,  $\text{C}_3\text{H}_5\text{Cl}_3$ , and a formate, but this again splits up with formation of a chloride of alkali-metal and dichloride of allylene,  $\text{C}_3\text{H}_4\text{Cl}_2$ . It is to the production of the last substance that the curious and valuable medicinal effects of butyl chloral are chiefly due.

DICHLORIDE OF ALLYLENE is very unstable, being gradually decomposed, even at ordinary temperatures, and acquiring an acid reaction and disagreeable odour. The proneness to change so marked in some samples of commercial chloroform, and the readiness with which the latter decomposes and becomes acid, are properties most probably due to the presence of dichloride of allylene. Its presence is probably due to the existence of aldehyde in the crude alcohol used for the preparation of the chloroform. By the action of chlorine the aldehyde is converted into butyl-chloral, and this, by subsequent contact with the chalk used for neutralisation, gives dichloride of allylene.

**Trichlor-acetic Acid.**  $\text{H}_3\text{C}_2\text{Cl}_3\text{O}_2$ , is a product of the action of oxidising agents on chloral. When equivalent quantities of chloral hydrate and potassium permanganate are cautiously mixed in concentrated solution, potassium trichlor-acetate is formed, and may be obtained in

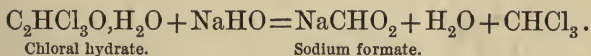
white silky crystals by filtering and evaporating the liquid. By the action of alkalies, trichlor-acetic acid yields chloroform and a carbonate.

## CHLOROFORM.

### Trichloro-methane. Methenyl trichloride.

*French.*—Chloroforme.  $\text{CHCl}_3$ .

Chloroform is generally manufactured by distilling dilute alcohol with hypochlorite and hydrate of calcium (bleaching powder and slaked lime). A complicated reaction ensues,\* and the product requires careful purification for the removal of secondary products. Chloroform is also prepared by distilling chloral hydrate with dilute alkali, when the following reaction occurs:—

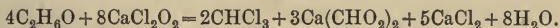


It is extremely probable that the dangerous and fatal effects occasionally attending the administration of chloroform are due to impurities in the commercial article. Hence, the careful preparation and thorough purification of chloroform are of great importance.

Chloroform is a colourless limpid liquid, of peculiar odour, and sweet but somewhat burning taste. The anæsthetic effects produced by inhaling its vapour are well known. Pure chloroform is not combustible, but when mixed with alcohol it burns with a smoky flame edged with green.

Chloroform is almost insoluble in water (·44 grammes in 100 c.c.), to which, however, it imparts a sweet taste. It is

\* The production of chloroform by the action of bleaching powder on alcohol may be represented by the following equation:—



Recent researches, however, have shown that the reactions which occur in practice are far more complicated (see note on page 164). It is probably on this account that pure methyl alcohol yields no chloroform on treatment with chlorine and an alkali. Acetone, on the other hand, may be substituted for alcohol in the preparation of chloroform.



miscible in all proportions with alcohol, ether, benzene, and carbon disulphide.

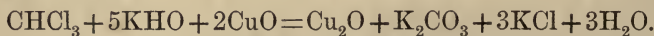
Chloroform possesses remarkable solvent properties, dissolving many organic bases, fats, wax, camphor, resins, india-rubber, guttapercha, pitch, iodine, bromine, and phosphorus.

Many important properties of chloroform are described on page 176, *et seq.*

DETECTION AND DETERMINATION OF CHLOROFORM.—As a rule, the detection of chloroform itself is less important than the recognition and estimation of other substances in presence of chloroform.

1. A very delicate method for the detection of chloroform in presence of large quantities of alcohol has been described by Dr Hofmann.\* All that is necessary is to add to the liquid to be tested some alcoholic soda and a little aniline. Either immediately or on gently warming the mixture, a strong and peculiar smell will be observed, due to the formation of benzo-isonitrile, ( $C_7H_5N$ ). Bromoform and iodoform also give the reaction, as also do chloral, trichlor-acetic acid, and all other bodies which yield either of the above products by treatment with alkalis. On the other hand, ethylidene chloride,  $C_2H_4Cl_2$ , gives no isonitrile under the same conditions. The test is so delicate that one part of chloroform dissolved in 5000 parts of alcohol may be detected with certainty by means of it.

2. The reduction of Fehling's alkaline copper solution is also a good and delicate test for chloroform, with which it reacts thus :—



When the solution is heated, the formation of the yellow-red cuprous oxide occurs very promptly. The reaction might probably be used for the determination of chloroform in the absence of other reducing agents. Chlor-ethylidene and alcohol do not interfere with the test.

\* *Deut. Chem. Ges. Ber.* iii. 769.

3. When chloroform vapour mixed with hydrogen is passed through a red-hot tube, it is decomposed with production of hydrochloric acid. This fact may be employed for the detection and estimation of chloroform. The sample should be boiled in a small flask through which a current of hydrogen is allowed to pass. The mixed hydrogen and chloroform vapour are caused to pass through a short length of heated combustion tube containing platinum wire gauze.

The products of the reaction are collected in a bulb tube containing water, and the hydrochloric acid produced is titrated with standard alkali, or precipitated with nitrate of silver. 109·5 parts of hydrochloric acid or 430·5 of chloride of silver represent 119·5 of chloroform.

This process is especially useful for the determination of small quantities of chloroform contained in other non-chlorinated liquids. It may be employed for the detection and estimation of chloroform in blood. When its detection only is required, a current of air may be substituted for the hydrogen. There is no occasion to heat the blood.

**Commercial Chloroform.**—According to some observers, chloroform, when quite free from alcohol, is liable to decomposition by light, especially in presence of moisture. Hence, alcohol is very commonly added as a preservative. According to Personne, however, samples liable to this change always contain chloro-carbonic ether,  $C_2H_5CO_2Cl$ . The alteration has also been attributed to the presence of dichloride of allylene. At any rate, certain specimens of chloroform, originally of good quality, on keeping become impregnated with hydrochloric and hypochlorous acids, and also with formic acid.

In addition to these impurities, resultant from decomposition, commercial chloroform may contain alcohol, aldehyde, and various chlorinated oils. These last are very injurious and even poisonous, and are detected and eliminated with considerable difficulty. Other products may

be present if the alcohol employed for the manufacture of the chloroform contained methyl or amyl compounds. Methylic alcohol is generally supposed to be capable of forming chloroform, but from experiments on the perfectly pure substance, this notion seems to have been disproved. Alcohol and aldehyde are sometimes added to chloroform in very considerable proportions. The adulteration of chloroform with ether and acetic ether has also been practised.

The presence of free chlorine and hypochlorous and hydrochloric acids in chloroform is recognised by shaking the sample with a solution of nitrate of silver, which in presence of either of the above impurities will produce a white precipitate.\* If the precipitate blacken on heating the presence of formic acid or aldehyde is indicated. Free chlorine and hypochlorous acid are distinguished from hydrochloric by their power of bleaching, instead of merely reddening, litmus, and of liberating iodine from a solution of pure iodide of potassium when the sample is shaken with it. The liberated iodine colours the chloroform reddish-violet.

Chloroform prepared from wood-spirit, or methylated spirit, is commonly called methylated chloroform. It is a mistake to suppose that the chloroform sold under this name has received an actual addition of wood-spirit, but such chloroform is liable to be much less pure than that obtained solely from ethylic alcohol. Chloroform prepared from methylated spirit is more difficult to purify than that made from pure alcohol, but a product is now manufactured from the former source, which appears to be equal in all respects to the dearer article.

Imperfectly purified methylated chloroform is specifically lighter than the pure substance, has an empyreumatic odour, and produces disagreeable sensations when inhaled. In some cases such chloroform seems actually poisonous, and produces general and rapid prostration. Such impure chloroform con-

\* Nitrate of silver gives no reaction with pure chloroform either in aqueous or in alcoholic solution.

tains several percentages of a chlorinated oil, lighter than water, and boiling at a much higher temperature than chloroform. A similar but different oil (heavier than water) is sometimes contained in much smaller quantity in chloroform prepared from alcohol containing no methyl compounds.

Dichloride of Ethylene,  $C_2H_4Cl_2$ , may be detected in chloroform by drying the sample by agitation with dry carbonate of potassium, and then adding metallic potassium. This does not act on pure chloroform, but in presence of the above impurity it produces chlor-ethylene,  $C_2H_3Cl$ , a gas of an alliaceous odour. It is very doubtful whether the substance in chloroform of the formula  $C_2H_4Cl_2$  is always dichloride of ethylene. It is probably more frequently the isomer dichlorethane or chlorinated ethyl chloride =  $CH_3CHCl_2$  (see page 158).

The presence of chloride of ethyl,  $C_2H_5Cl$ , in chloroform is best recognised by distilling the sample with water in a water-bath. The first portions of the distillate will have a distinct smell of the foreign body.

Chloroform is not soluble in strong sulphuric acid, and, when pure, is not acted on until after the lapse of some time, when shaken with that reagent. Any darkening of the acid which occurs may be due to the presence of aldehyde, wood-spirit, &c. Pure chloroform floats on strong sulphuric acid with a contact surface convex downwards, but if impure gives a plane contact surface. The presence of chlorinated oils also causes a brown coloration with sulphuric acid.

The boiling point of chloroform is a valuable indication of its purity. Pure chloroform boils at  $60.8^\circ C$ . The presence of  $\frac{1}{2}$  per cent. of alcohol reduces the boiling point to  $59.8^\circ$  or  $60^\circ C$ . A boiling point higher than  $61^\circ C$ . indicates the presence of amyl or butyl compounds. In some cases the boiling point of the last portions distilled is as high as  $70^\circ C$ .

Pure chloroform volatilises entirely without disagreeable smell. The impurities are generally less volatile. Many



kinds of impurity in chloroform may be readily recognised by the disagreeable odour left on the evaporation of the sample from a cloth or filter-paper soaked with it.

Pure chloroform is not *visibly* altered when heated with solution of potassa, though it is slowly acted on with formation of a formate and chloride of the alkali-metal. In alcoholic solution this reaction occurs rapidly. In presence of aldehyde or acetone, the solution of potassa becomes coloured brown.

Any considerable admixture of ether with chloroform will be indicated by the inflammability and diminished density of the liquid.

When perfectly pure, chloroform appears to be much more stable than when containing foreign matters. Moisture accelerates its decomposition. One-eighth per cent. of alcohol is said to have a greater preservative effect than a larger proportion.

The proportion of alcohol present in chloroform can in some cases be ascertained from the density. According to C. Remys,\* pure chloroform has a density of 1·500 at 15° C. The presence of  $\frac{1}{8}$  per cent. of alcohol reduces the density by ·002, and  $\frac{1}{2}$  per cent. by ·008.† Chloroform containing amyl or butyl compounds has a higher density than 1·500.

The following table by M. Besnou, gives the densities of various mixtures of alcohol and the purest *commercial* chloroform. The temperature of the experiments was 4·5° C.

Specific gravity.	Chloroform. Per Cent.	Alcohol. Per Cent.
1·4945	100·0	0·0
1·4908	99·5	0·5
1·4874	99·0	1·0
1·4845	98·5	1·5
1·4772	97·5	2·5
1·4602	95·0	5·0
1·4262	90·0	10·0
1·4090	87·5	12·5

\* *Archiv. der Pharm.* [3] v. 31.

† According to A. H. Mason, chloroform containing 1 per cent. of alcohol has a density of 1·497 at 15·5° C.

The chloroform of the British Pharmacopœia has a density of 1.49. Chloroform of low density probably sometimes contains ether.

Caustic potash is quite insoluble in dry chloroform, but dissolves sensibly in presence of water or alcohol. If therefore a piece of stick potash be fused on a loop of platinum wire, and introduced into some of the chloroform contained in a dry test-tube, the liquid will not acquire the power of turning red litmus paper blue, unless water or alcohol be present. If more than a trace of alcohol be present, the decanted chloroform, when shaken with water, yields a liquid which gives a blue precipitate with a solution of sulphate of copper. To use this test with certainty to distinguish between water and alcohol, the sample must be first shaken with recently ignited potassium carbonate. This will remove water but not alcohol, so that if the chloroform still possesses the power of dissolving caustic potash, alcohol must be present.

When the quantity of alcohol in chloroform exceeds 1 or 2 per cent., the proportion may be determined with tolerable accuracy by shaking 20 c.c. of the sample in a graduated tube with 80 c.c. of water. If the chloroform be pure it will sink to the bottom in clear globules, but in the presence of alcohol the liquid and the surface of the drops will become dim and opalescent. The reduction in the volume of the chloroform shows the proportion of alcohol in the amount taken. The addition of a few drops of solution of potassa destroys the meniscus, and enables the volume to be read more accurately. The aqueous liquid may be tested for sulphuric acid by barium chloride, for free chlorine or hypochlorous acid by starch and iodide of potassium, and for hydrochloric acid by silver nitrate.

A reliable test for alcohol in chloroform (which might probably be made to give quantitative results), has been described by M. Besnou. He takes a few milligrammes of powdered potassium bichromate and places it in a narrow test-tube.

He next adds four or five drops of concentrated sulphuric acid, and stirs well, and then adds three or four drops of water to dissolve the liberated chromic acid. Lastly, he pours in 3 or 4 c.c. of the sample of chloroform, shakes quickly for twenty or thirty seconds, and leaves the whole to repose; very soon the deep-green colour of the chromic chloride appears (if the proportion of alcohol amounts to 5 per cent.), and is deposited in a distinct layer at the bottom, while the upper part is barely coloured a pale-green. If the chloroform be pure, the liquid is scarcely tinged of a greenish-yellow, and no lower layer separates. Ether reacts in the same manner as alcohol.

Roussin\* has proposed to use dinitro-sulphide of iron as a test for alcohol, aldehyde, amylic alcohol, ether, or wood-spirit in chloroform; in presence of either of these impurities the liquid acquires a dark colour, but remains colourless when pure. Dinitro-sulphide of iron is prepared by slowly adding ferric sulphate to a boiling mixture of ammonium sulphide and potassic nitrite as long as the precipitate at first produced continues to dissolve, and subsequently filtering the solution.

Stoedeler has suggested fuchsine for detecting alcohol in chloroform. The sample becomes coloured red if alcohol be present, the depth of colour varying with the proportion of alcohol. The author found† that even after agitation with chloride of calcium, the chloroform became coloured on adding fuchsine, but by agitating the sample with one-fifth of its bulk of strong sulphuric acid, and subsequently removing traces of the latter by shaking with dry precipitated carbonate of barium, the chloroform was obtained so pure as to give only a very slight coloration with fuchsine. This purified chloroform could then be used in a similar manner to the ether on page 135 for determining small proportions of alcohol in chloroform. Chloroform may also be purified from water, alcohol,

\* *Journ. Pharm.* [3] xxxiv. 206.

† *Analyst*, 1877, page 97.

and ether, by agitating with sulphuric acid as above, separating the acid, and shaking the chloroform with a strong solution of sodium carbonate, and, lastly, distilling it over freshly burnt lime.

The most delicate test for the presence of alcohol in chloroform is that of A. Lieben, as modified by Hager. For the details of the mode of applying it, see page 80. It depends on the fact that alcohol under the influence of iodine and an alkali yields iodoform, the properties of which are described below.

**Bromoform**,  $\text{CHBr}_3$ , closely resembles chloroform, but boils at  $150^\circ\text{--}152^\circ\text{C}$ . Its density is 2.9 at  $12^\circ\text{C}$ ., or, according to E. Schmidt, 2.775 at  $14.5^\circ\text{C}$ . It solidifies at  $-9^\circ\text{C}$ .

Caustic potash converts bromoform into chloride and formate of potassium. By the action of alcoholic potash gas is evolved, consisting of one volume of carbon monoxide and three of ethylene; thus—



Bromoform is not unfrequently present in commercial bromine, even to the extent of 10 per cent. It may be detected by fractional distillation of the bromine on the water-bath, or by treating the sample with excess of solution of potassium iodide, and then adding sufficient sodium thiosulphate (hypo-sulphite) to take up the iodine set free. The characteristic odour of bromoform then becomes apparent.

**Iodoform**,  $\text{CHI}_3$ , is produced in Lieben's test for alcohol (page 80). It is a yellow, shining, crystalline solid, having an odour resembling saffron or a solution of iodine in chloroform. It volatilises at ordinary temperatures. Iodoform is almost insoluble in water (1 part in 13000) or glycerin, but is more soluble in alcohol (1 part in 80), and very soluble in ether and chloroform. In its chemical reactions it closely resembles chloroform. Its microscopic appearance is very characteristic, its usual forms being hexagonal plates, stars, and rosettes.

When heated gently, iodoform volatilises without change, but a strong heat decomposes it.



Iodoform ought to dissolve completely in boiling alcohol, but should be insoluble in brine. It should leave no residue on ignition.

**Methene Dichloride.** Bichloride of methylene.  $\text{CH}_2\text{Cl}_2$ .  
—This substance is the second of the products arising from the action of chlorine on marsh gas, the following being the complete series :—

- $\text{CH}_4$ , Methane, or marsh gas.  
 $\text{CH}_3\text{Cl}$ , Chloromethane, or methyl chloride.  
 $\text{CH}_2\text{Cl}_2$ , Dichloromethane, or methene dichloride.  
 $\text{CHCl}_3$ , Trichloromethane, or chloroform.  
 $\text{CCl}_4$ , Carbon tetrachloride.

Methene dichloride is usually prepared by distilling a mixture of one part of methylic alcohol, two of common salt, and three of sulphuric acid. Methyl chloride is obtained as a gas of a sweetish taste, and ethereal odour. This is passed into a large glass globe, together with chlorine, and the mixture exposed to day-light. The products pass through two Woulffe's bottles, and then into a flask surrounded by a freezing mixture. The former chiefly contain chloroform, while the methene dichloride condenses in the flask in a pure state.

Bichloride of methylene, being troublesome to prepare, is more expensive than chloroform, and hence the latter liquid is sometimes substituted and sold for the more valuable anæsthetic.\* The following are the chief characters by which they may be distinguished from each other.

	Chloroform.	Methene Dichloride.
1. Density at $17^\circ \text{C}$ .	1.492	1.360
2. Boiling point	$60.8^\circ \text{C}$ .	$41^\circ \text{C}$ .
3. Character of flame when ignited	Burns with difficulty with green - edged flame	Burns with a smoky flame
4. Iodine dissolves with	Reddish violet colour	Brown colour

\* Bichloride of methylene is a powerful anæsthetic, but is said to have a very depressing effect.

The isomer of bichloride of methylene, chlorinated methyl chloride,  $\text{CH}_2\text{Cl}_2$ , boils at  $30.5^\circ \text{C}$ ., and has a density of 1.344.

A mixture of alcohol and chloroform has been substituted for bichloride of methylene. By shaking the sample with water the alcohol would be dissolved, and the chloroform would then be recognisable by its density, &c.

## ACID DERIVATIVES OF ALCOHOLS, AND VEGETABLE ACIDS.

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THIS numerous and important class of organic bodies contains a great variety of acids, some of which occur ready formed in plants, and the synthesis of which has not been hitherto effected in the laboratory. In addition to these, there are many which can also be obtained artificially, and others again which are purely artificial products.

All the acids treated of in this division are compounds of carbon, hydrogen, and oxygen. When a metallic salt of one of them is ignited in the air it leaves the metal, sometimes in the free state (as the salts of silver) but more frequently in the form of oxide. If the organic salt be a compound of one of the metals of the alkalies or alkaline-earths, on ignition in the air there is obtained the corresponding carbonate. If this be dissolved in standard acid, the diminution in the acidity of the liquid will be equivalent to the organic acid previously present. This fact is often utilised for the indirect determination of vegetable acids (see methods 3 and 5, p. 190), and is applicable in presence of sulphates, chlorides, &c. The substance or solution must be neutral in reaction before ignition, or, if not so, must be brought into that condition. Nitrates interfere, as, on ignition in contact with organic matter they yield carbonates, together with decided traces of cyanides.

The following table shows the manner in which the neutral solutions of the potassium or sodium salts of the acids of this division are precipitated by cold neutral solutions of barium, calcium and ferric chlorides, lead acetate, and silver nitrate. In all cases the reactions refer to moderately concentrated

solutions of the salts. When the precipitate is somewhat soluble in water, so as to render its production questionable, the letter P is placed within parentheses. S signifies that the substance sought is soluble, and hence that no precipitate is obtained. Except when otherwise mentioned the precipitates are white. In addition to the reactions with the above metallic solutions, columns are added showing the reactions of the organic acids with other important reagents. R signifies "Reduction," and 0 "no effect":—

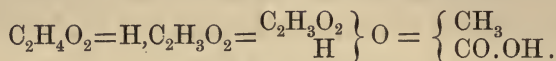
TABLE SHOWING REACTIONS OF NEUTRAL SOLUTIONS OF VEGETABLE ACIDS WITH REAGENTS.

Name of Salt in Solution.	With Barium Chloride.	With Calcium Chloride.	With Ferric Chloride.	With Lead Acetate.	With Silver Nitrate.	With Fehling's Solution.	With Permanganate in Cold Acid Solution.	With Concentrated Sulphuric Acid.	Remarks.
Acetate .	S	S	Red colour.	S	(P)	0		Smell of acetic acid.	Ag salt not reduced on heating.
Formate .	S	S	Red colour.	S	(S)	...	R	CO evolved.	Ag salt or solution reduced on heating.
Oxalate .	P	P	S	P	P	0	R	CO+CO <sub>2</sub> evolved.	A yellow precipitate sometimes occurs on adding FeCl <sub>3</sub> .
Lactate .	S	S	S	S	S	0	R	CO evolved brown colour.	See pages 228, 229.
Succinate .	(P)	(S)	Red-brown precipitate.	P	P	0	0	No change.	Ba and Ca salts precipitated on adding alcohol.
Malate .	S	(S)	S	P	P	0	R	Darkened.	Ca salt insoluble in dilute alcohol.
Tartrate .	P	P	S	P	P	0	R	Charring.	Ag salt reduced on heating.
Citrate .	P	P	S	P	P	0	0	CO evolved brown colour.	Ca salt precipitated on boiling and redissolved on cooling.
Aconitate .	(P)	(P)	...	P	P	...	...	...	Ca salt is soluble in 100 parts of water.
Meconate .	(P)	P	Red colour.	P	P	...	...	...	Action of oxidising agents not recorded.
Gallate .	(S)	(P)	Deep blue colour.	P	Reduced on heating.	0	R	Red brown colour.	Salts darken rapidly in presence of alkali.
Pyrogallate	...	Red colour turning brown.	Red colour.	P	Reduced.	R	R	...	Salts darken rapidly in presence of alkali.
Gallotannate	...	P	Blue-black precipitate.	P	Reduced on heating.	R	R	Purple colour and charring.	Almost impossible to obtain neutral solutions.



**ACETIC ACID.****Hydrogen Acetate.**

*French*—Acide acétique. *German*—Essigsäure.



Acetic acid exists ready formed in certain plants, and is a frequent product in chemical reactions. It is produced by the acetic fermentation of sugar, and by the limited oxidation of alcohol. In commerce, the largest quantity is obtained from the products of the distillation of wood, the crude pyro-ligneous acid being neutralised with lime, and the resultant salt distilled with sulphuric or hydrochloric acid. Pure acetic acid is a colourless crystalline solid, known in commerce as "Glacial Acetic Acid." The pure substance melts at  $16.7^\circ \text{C}$ ., but a small admixture of water greatly lowers its melting point, as shown in following table by F. Rudorff.\*—

Solidifying Point. °C.	Water to 100 parts of real $\text{C}_2\text{H}_4\text{O}_2$ .	Solidifying Point. °C.	Water to 100 parts of real $\text{C}_2\text{H}_4\text{O}_2$ .
+16.70	0.0	6.25	8.0
16.65	0.5	5.30	9.0
14.80	1.0	4.30	10.0
14.00	1.5	3.60	11.0
13.25	2.0	2.70	12.0
11.95	3.0	-0.20	15.0
10.50	4.0	-2.60	18.0
9.40	5.0	-5.10	21.0
8.20	6.0	-7.40	24.0
7.10	7.0		

Pure acetic acid boils at  $119^\circ \text{C}$ ., and may be distilled unchanged. The hydrate,  $\text{C}_2\text{H}_4\text{O}_2 \cdot \text{H}_2\text{O}$ , boils at  $104^\circ \text{C}$ . For peculiarities in the strength of distilled acetic acid, see page 212, *et seq*.

Acetic acid is miscible in all proportions with water, alcohol,

\* *Pharm. Journ.* 3d series, ii. 241.

and ether. It dissolves many essential oils, camphor and resins, phenols, gelatin, and many metallic salts insoluble in water.

Addition of water to glacial acetic acid causes evolution of heat, and a contraction in volume ensues till about 20 per cent. of water has been added, when a hydrate is formed of the composition,  $C_2H_4O_2, H_2O$ . Acid of this strength has a higher density than the glacial acid, so that either concentration or dilution of the hydrate  $C_2H_4O_2, H_2O$ , causes a diminution of gravity. This fact must not be lost sight of in estimating acetic acid by its density. In fact, the density is not to be relied on for the determination of acetic acid in concentrated solution, though it is of service for the dilute acid.

The densities of mixtures in various proportions of acetic acid and water have been determined by Mohr and by Oudemanns. According to the latter chemist, Mohr's observations were made on an impure acid containing about 5 per cent. of water.

The following table shows the density of acetic acid of different strengths, according both to Oudemanns and to Mohr, the temperature in each case being  $15^\circ C.$  ( $=59^\circ F.$ ):—

$C_2H_4O_2$ Per cent.	Density.		$C_2H_4O_2$ Per cent.	Density.	
	Oudemanns.	Mohr.		Oudemanns.	Mohr.
1	1·0007	1·001	21	1·0298	1·029
2	1·0022	1·002	22	1·0311	1·031
3	1·0037	1·004	23	1·0324	1·032
4	1·0052	1·005	24	1·0337	1·033
5	1·0067	1·007	25	1·0350	1·034
6	1·0083	1·008	26	1·0363	1·035
7	1·0098	1·010	27	1·0375	1·036
8	1·0113	1·012	28	1·0388	1·038
9	1·0127	1·013	29	1·0400	1·039
10	1·0142	1·015	30	1·0412	1·040
11	1·0157	1·016	31	1·0424	1·041
12	1·0171	1·017	32	1·0436	1·042
13	1·0185	1·018	33	1·0447	1·044
14	1·0200	1·020	40	1·0523	1·051
15	1·0214	1·022	50	1·0615	1·061
16	1·0228	1·023	60	1·0685	1·067
17	1·0242	1·024	70	1·0733	1·070
18	1·0256	1·025	79	1·0748	1·0735
19	1·0270	1·026	80	1·0748	1·0735
20	1·0284	1·027	90	1·0713	1·0730
			100	1·0553	1·0635

From this table it will be seen that acid of 100 per cent. and acid of about 43 per cent. have the same density.

The acetic acid of the British Pharmacopœia contains 33 per cent. by weight of real acid ( $C_2H_4O_2$ ), and has a density of 1.044.

Dilute acetic acid, B. P., is made by diluting one measure of the above with seven of water, has a gravity of 1.006, and contains 4.27 per cent. of real acetic acid ( $C_2H_4O_2$ ).

The glacial acetic acid of the Pharmacopœia is said to have a density of 1.065 to 1.066, and to contain at least 98.8 per cent. of real acid.\* It should crystallise at  $1.1^\circ C.$  ( $=34^\circ F.$ ), and remain solid till heated above  $8.9^\circ C.$  ( $=48^\circ F.$ ).

Cold acetic acid is not inflammable, but the vapour given off by the boiling acid burns with a blue flame. Concentrated acetic acid is a powerful caustic. It does not redden litmus until mixed with water.

Acetic acid is not readily attacked by reagents. Permanganate and nitric acid have no effect on it. Chlorine converts it into chlor-acetic acid,  $H, C_2H_2ClO, O$ .

DETECTION OF ACETIC ACID AND ACETATES.—Most of the acetates are soluble in water. A few oxy-acetates ("basic" acetates) are insoluble, and the neutral argentic and mercurous salts are sparingly soluble. Hence, acetic acid cannot be determined or readily detected by precipitation. Free acetic acid may generally be recognised by its smell and other physical properties, or it may be neutralised by caustic soda, and examined by the following tests.

Metallic acetates give the following reactions:—

1. Subjected to dry distillation, acetone,  $C_3H_6O$ , is given off, having a highly characteristic odour (see page 70).

\* If Oudemann's density table be correct, these characters are incompatible. All the B. P. percentages appear, however, to be calculated from Mohr's table. On the other hand, I have shown (*Analyst*, June 1878, page 268) that inconsistencies exist in the part of Oudemann's tables referring to dilute acid, though it is decidedly preferable to Mohr's. Of course these discrepancies are quite independent of the well-known abnormal density of acetic acid of a certain strength.

2. Heated in the solid state in admixture with arsenious oxide ( $\text{As}_2\text{O}_3$ ), acetates give an alliaceous and very characteristic smell of *cacodyl*,  $\text{AsC}_2\text{H}_5$ , which is very poisonous.

3. Heated with sulphuric or phosphoric acid, acetic acid is given off.

4. Heated with rectified spirit of wine (not methylated) and concentrated sulphuric acid, a fragrant and characteristic odour of *ethyl acetate* (acetic ether) is produced (see page 145).

5. The neutral solution, on treatment with ferric nitrate or chloride (*avoiding excess*), gives a deep-red liquid containing ferric acetate. This is decomposed on boiling, the liquid becoming colourless and depositing reddish-brown ferric oxy-acetate. The reaction is imperfect if the iron solution be added in excess. The cold red liquid is not decolorised on addition of mercuric chloride (distinction between acetates and thiocyanates), and is not taken up by ether on agitation (distinction from thiocyanates); the colour is destroyed on addition of cold dilute sulphuric or hydrochloric acid (distinction from meconates).

6. Insoluble or basic acetates may be decomposed by boiling solution of sodium carbonate, when the acetate will be found in the filtered liquid as a sodium salt.

Acetates of alkaloids and nitrogenised organic bases, as a rule, respond to the foregoing tests, but acetates of the alcohol radicals (acetic ethers) do not usually do so. They are readily decomposed, however, by digestion with alcoholic potash or soda, and, after distilling off the resultant alcohol, the residual liquid may be examined for an alkaline acetate (see also "compound ethers," page 140).

#### DETERMINATION OF ACETIC ACID AND ACETATES.

1. When simply in admixture with water, acetic acid may be determined by the density of the liquid (see page 187).

2. In the absence of other free acids, free acetic acid may be determined volumetrically by titrating the liquid with decinormal alkali. Litmus solution may be used as an indicator,



or, when dark-coloured liquids are to be assayed, litmus *paper* may be substituted for it.

A convenient mode of working in some cases consists in the addition of a few drops of sulphate of copper solution, the production of a permanent turbidity being taken as the point of neutrality. The results agree closely with those obtained by the use of litmus. The numbers obtained by the titration of acetic acid with either of the above indicators are about 0.1 per cent. below the truth, owing to the alkaline reaction possessed by acetates of neutral constitution.

[For the titration of mineral acids in presence of free acetic acid, the use of methyl-aniline-violet has been recommended. Unfortunately, the dark colour of the liquid (vinegar), in which such a determination is usually required, renders its employment very difficult, and, apart from this objection, the author has not found its value as an indicator as great as has been claimed for it.]

3. Like the corresponding salts of other organic acids, the acetates of the metals of the alkalis and alkaline-earths are converted into carbonates on ignition. Hence, in the absence of other organic acids, or of nitrates, &c., the amount of acetate originally present may be ascertained by titrating the residue of the ignition with standard acid. Each c.c. of normal acid required for neutralisation represents .060 grammes of  $C_2H_4O_2$  in the sample.

4. The acetates of such metals as are completely precipitated by sodium carbonate (*e.g.*, calcium, lead, iron) may be decomposed by a known quantity of it, the liquid well boiled, filtered, and the filtrate titrated with standard acid. The loss of alkalinity represents the acetic acid originally present as an acetate. Before employing this method, the solution must be exactly neutralised, if not neutral already.

5. In presence of salts other than acetates the last method is valueless, but the following modification may be employed:—The excess of carbonate of sodium is exactly neutralised by

hydrochloric acid, the liquid evaporated to dryness, the residue ignited, and the resultant carbonate titrated with standard acid. Each c.c. of standard acid represents '060 grammes of acetic acid. Other organic acids will be estimated as acetic acid.

6. Free acetic acid may also be determined by adding excess of pure precipitated barium carbonate to the solution. The liquid is well boiled, filtered, and the barium in the filtrate precipitated by dilute sulphuric acid. 233 parts of  $\text{BaSO}_4$  obtained, represent 120 of  $\text{HC}_2\text{H}_3\text{O}_2$  in the sample taken. This process is applicable in presence of oxalic, phosphoric, sulphuric, and other *free* acids forming insoluble barium salts, but is useless in presence of soluble oxalates, phosphates, sulphates, &c. The method is available in presence of alkaline chlorides, &c., but not in presence of free hydrochloric acid, unless the solution be previously treated with excess of argentic sulphate. Acetates and chlorides of metals of the alkalis and the alkaline-earths do not interfere, but acetates and other salts of iron, aluminium, and other metals precipitable by barium carbonate must be absent.

7. The determination of acetic acid in acetates is best effected by distilling the salt to dryness with a moderate excess of sulphuric acid. Water should then be added to the contents of the retort, and the distillation repeated. A third, and even a fourth, distillation will sometimes be necessary, as the last traces of acetic acid are volatilised with extreme difficulty.

In presence of hydrochloric acid or chlorides, excess of sulphate of silver should be added before commencing distillation.

In presence of sugar or other bodies liable to decomposition by sulphuric acid, phosphoric acid should be substituted for the latter. Care should be taken that the phosphoric acid used is free from nitric and other volatile acids.

This plan is of service for the determination of acetic acid

in wine. A measured quantity of the sample is neutralised with baryta, the alcohol distilled off, phosphoric acid added to the residue, and the distillation repeated, the process being carried nearly to dryness. To obtain the last traces of acetic acid, water should be added and the distillation repeated.

8. When great accuracy is not required, and the amount of fixed matters present is not very large, or of such nature as to interfere, M. Duclaux's observation may be usefully applied. This chemist found that when 110 c.c. of a liquid containing acetic acid were distilled in a retort of 250 to 300 c.c. capacity till exactly 100 c.c. had passed over, the distillate invariably contained 79·8 per cent. of the total acetic acid present (see page 213).\*

For the estimation of acetic acid in presence of its homologues, see page 212, *et seq.*

**Commercial Acetic Acid** is liable to contain—

1. **SULPHURIC ACID** and **SULPHATES**, indicated and determined by addition of barium chloride, which in their presence throws down white barium sulphate.†

2. **SULPHUROUS ACID**, indicated by adding barium chloride in excess, filtering from any precipitate, and adding bromine water to the clear filtrate. An additional precipitate of barium sulphate indicates the previous presence of sulphurous acid, and from its weight the amount of impurity can be calculated.

3. **HYDROCHLORIC ACID** and **CHLORIDES**, detected and estimated by addition of nitrate of silver.

4. **COPPER AND LEAD**, detected by evaporating a considerable bulk of the sample to a small volume, diluting with water, adding a few drops of hydrochloric acid and passing

\* I have attempted to apply this method to the assay of calcium acetate. Although the proportion of total acetic acid which was found in the distillate was tolerably constant, the percentage was considerably under that found by M. Duclaux.

† For the detection and estimation of small amounts of free sulphuric and hydrochloric acids in acetic acid and vinegar, see page 198, *et seq.*



sulphuretted hydrogen, which produces a black or brown coloration or precipitate in presence of lead or copper. If much organic matter be present, the evaporation should be carried to dryness, and the residue ignited in porcelain. The heavy metals are dissolved out of the residue by a few drops of nitric acid, and the diluted liquid tested with sulphuretted hydrogen. A more delicate test for copper is the red-brown precipitate or coloration produced by potassium ferrocyanide. If iron be present in such quantity as to give a blue precipitate and thus interfere with the reaction, it must first be removed by addition of bromine water and excess of ammonia, and copper sought for in the filtrate after acidifying with acetic or hydrochloric acid. Samples of pickles suspected to be coloured with copper should be moistened with sulphuric acid, ignited, and the ash dissolved in nitric acid, and tested in acid solution with potassium ferrocyanide, after separation of the iron and phosphates with ammonia. The copper can be determined by precipitation on the inside of a platinum crucible by a current from one cell of Grove's battery, or by precipitation with a stick of cadmium. Tin and zinc are occasionally met with in acetic acid and vinegar (see pages 101 and 201).

5. SALTS OF CALCIUM: detected by partially neutralising the solution with ammonia, and adding ammonium oxalate, which will produce a white precipitate of calcium oxalate.

6. EMPYREUMATIC AND INDEFINITE ORGANIC BODIES: detected by exactly neutralising the acid with carbonate of sodium and tasting and smelling the warmed liquid. The neutralised acid gives a precipitate when heated to boiling with ammonio-nitrate of silver, if the above impurities are present.\* By distilling the acid with a little potassium bichromate, these impurities may be entirely removed.

\* A sample of glacial acetic acid containing fully 99 per cent. of  $C_2H_4O_2$  was observed by V. Meyer to give a deep red coloration with aniline. This property he traced to the presence of furfur-aldehyde or furfurol,  $C_5H_4O_2$ , and from the depth of the coloration produced estimated the proportion of the impurity to be 0.108 grammes per litre of the acid.



7. GENERAL FIXED IMPURITIES: detected and estimated by evaporation of a known measure of the sample to dryness.

**Pyroligneous Acid.** Wood Vinegar.

*French*—Acid Pyroligneux, or Vinaigre de Bois.

*German*—Holz-essig, or Holz-säure.

This name is applied to the crude acetic acid obtained by the distillation of wood. It is exceedingly impure. The only valuable constituent is the acetic acid, which, even when purified, often contains sufficient tarry and empyreumatic products to indicate its origin. These may be entirely removed, however, by redistilling the acid with potassium bichromate.

The strength of pyroligneous acid may be ascertained by titration with standard alkali, but the liquid is frequently too dark in colour to permit of the end-reaction being readily observed (see page 190). Sulphates and acetates of calcium and sodium are frequently present. In the absence of sulphates, pyroligneous acid is best assayed by treatment with excess of barium carbonate, with estimation of the dissolved barium as sulphate. (See page 191.)

Pyroligneous acid varies much in strength according to the kind and state of division of the wood used for distillation, and is also affected by the construction of the retorts. Lop-wood yields stronger acid and less tarry and resinous matters than spent dye-woods and sawdust, even though the same kind of wood be employed.

Pyroligneous acid from finely-divided wood has a density of 1.040 to 1.045, and contains, on an average, about  $4\frac{1}{2}$  per cent. of real acetic acid ( $\text{H}_4\text{C}_2\text{H}_3\text{O}_2$ ). The product of the distillation of lop-timber contains an average of  $7\frac{3}{4}$  per cent. of real acid.

**Vinegar.** *French*—Vinaigre. *German*—Essig.—Vinegar is a more or less coloured liquid, consisting essentially of impure dilute acetic acid. The agreeable aromatic smell is doubtless due to characteristic ethers. The "vinegar" of the British Pharmacopœia has a density of 1.017 to 1.019, and contains at least 5.4 per cent. by weight of real acetic acid

( $C_2H_4O_2$ ). The specific gravity of vinegar is of no value as an indication of its strength in acetic acid, as the proportion of extractive matter varies much in vinegar from various sources. The "proof vinegar" of the Excise contains about 5 per cent. of acetic anhydride ( $C_4H_6O_3$ ), or 6 per cent. of real acid, and has a density of 1.019. In commerce, vinegars are distinguished by the number of grains of pure dry carbonate of sodium required for the neutralisation of one fluid ounce. Thus, "proof vinegar" is known as "No. 24," from the fact that 24 grains of  $Na_2CO_3$  are required for the neutralisation of one ounce. The weaker qualities are Nos. 22, 20, and 18. As 60 grains of real acetic acid, or 51 of acetic anhydride, are neutralised by 53 of sodium carbonate, the number of grains of the real acid contained in each fluid ounce of the vinegar can be ascertained by multiplying the "number" of the sample by  $\frac{60}{53} = 1.132$ . If the "number" be multiplied by the factor .259, the product will be the parts by weight of real acid ( $H, C_2H_3O_2$ ) in 100 measures of the vinegar.

Vinegar containing less than 3 per cent. of real acetic acid may be regarded as diluted with water, or at any rate as unfit for use.

The titration of vinegar by a standard alkali is difficult in presence of much colouring matter. In such cases, the liquid should be diluted and litmus paper employed for indicating the end of the reaction, instead of adding litmus solution to the sample to be tested. Sulphate of copper may be conveniently employed as an indicator. In extreme cases, the vinegar may be distilled, and the distillate titrated.

Other methods of determining the acetic acid contained in vinegar are given on page 189, *et seq.*

WINE-VINEGAR varies in colour according as its origin was white or red wine, the former being most esteemed. It contains 8 to 10 per cent. of real acetic acid ( $HC_2H_3O_2$ ), has a low density (1.014 to 1.022), and an extract varying from 1.7 to 2.4 per cent. (average 2.05). If the "extract" or residue left

on evaporation be treated with alcohol, nearly everything dissolves except a granular residue of tartar, while vinegars made from malt or sugar leave a more or less glutinous residue, only sparingly soluble in alcohol. The amount of "tartar" (acid tartrate of potassium) contained in *wine-vinegar* averages 0.25 per cent. Its presence is peculiar to wine-vinegar. The tartar may be proved to be such by pouring off the alcohol and dissolving the residue in a small quantity of hot water. On cooling the aqueous solution, and stirring the sides of the vessel with a glass rod, the acid tartrate of potassium will be deposited in streaks in the track of the rod. An addition of an equal bulk of alcohol makes the reaction more delicate. Tartaric acid is occasionally added to vinegar as an adulterant, in which case the residue left on evaporation at a steam-heat is viscous and highly acid. By treatment with proof-spirit any free tartaric acid is dissolved, and may be detected in the solution by adding a solution of acetate of potassium in proof-spirit, and stirring with a glass rod. In presence of tartaric acid, streaks, and probably a distinct precipitate, of acid potassium tartrate will be produced. By treating the precipitate as described on page 265, the amount of free tartaric acid in the vinegar can be determined.

CRAB-VINEGAR, made from the crab-apple, is well known in Wales and the adjacent counties.

CIDER-VINEGAR, is yellowish, has an odour of apples, a density of 1.013 to 1.015, and contains  $3\frac{1}{2}$  to  $4\frac{1}{2}$  per cent. of acetic acid. On evaporation to dryness it yields about 1.5 per cent. of mucilaginous extract, smelling and tasting of baked apples, and containing malic but no tartaric acid. Cider-vinegar gives slight precipitates with barium chloride, silver nitrate, and ammonium oxalate. Perry-vinegar presents similar characters.

BEER- AND MALT-VINEGARS have a high density (1.021 to 1.025), and yield 5 to 6 per cent. of extract on evaporation to dryness. The acetic acid varies from 3 to 6 per cent. Chloride of barium and nitrate of silver frequently give considerable



precipitates, owing to the presence of sulphates and chlorides in the water used in the manufacture. (See note on page 198.)

GLUCOSE- OR SUGAR-VINEGAR usually contains glucose, dextrin, and calcium sulphate. Hence it reduces Fehling's copper solution, and gives abundant precipitates with barium chloride and ammonium oxalate, and frequently with silver nitrate also. When mixed with two or three times its volume of strong alcohol, glucose-vinegar gives a precipitate of dextrin. It is best to concentrate the sample before applying this test. Glucose is best detected and determined by evaporating 50 c.c. of the sample to a syrup and adding alcohol. The liquid is filtered, decolorised by boiling with animal charcoal, again filtered, the alcohol boiled off, and the glucose estimated by Fehling's copper solution. Glucose-vinegar is rarely used alone, but is employed (especially in France) for adulterating wine-vinegar.

ARTIFICIAL VINEGAR is sometimes made by mixing wine and acetic acid (often pyroligneous). Such vinegar gives off inflammable vapours of alcohol when boiled. Another factitious vinegar is made by diluting acetic acid to the strength of proof-vinegar, colouring it with burnt sugar, and flavouring it with a little acetic ether.

WOOD-VINEGAR is a name sometimes applied to pyroligneous acid. (Page 194.)

AROMATIC VINEGAR is a product obtained by distilling a metallic acetate, usually crystallised cupric acetate. The presence of acetone imparts an agreeable aroma. A small addition of camphor or essential oil is often made.

Very weak vinegar is liable to a putrid fermentation, to prevent which the addition of 1 gallon\* of sulphuric acid to 1000 gallons of vinegar was permitted by an Excise regulation.

\* This proportion of 1 gallon to 1000 is often erroneously stated at 0.1 per cent., whereas the true proportion resulting from the above admixture is of course about 0.185 parts by weight of sulphuric acid, or nearly twice as much as is generally assumed.



This addition is now known to be unnecessary with good vinegar, and is abandoned by the best makers, though the practice is by no means obsolete, and the legal proportion of sulphuric acid is occasionally largely exceeded.

**DETECTION OF MINERAL ACIDS IN VINEGAR.**—For effecting this various tests have been devised, but the majority are either untrustworthy or are deficient in delicacy. Some are applicable to the detection of sulphuric acid only, while others include hydrochloric and other mineral acids also. The employment of chloride of barium and nitrate of silver for the detection of sulphuric and hydrochloric acids respectively has led several analysts into error, owing to the natural presence of sulphates and chlorides in the water employed in the manufacture of the vinegar.\*

Another circumstance which complicates the question is, that the addition of a mineral acid in moderate quantity

\* A remarkable water of this character is employed by Messrs Hill & Evans of Worcester. The following analysis of it was made in 1874 by Dr Letheby:—

Silica, alumina, and oxide of iron	.	1.09 grains per gallon.
Carbonate of calcium	. . . . .	15.68       ,,
Carbonate of magnesium	. . . . .	1.43       ,,
Sulphate of calcium	. . . . .	144.16     ,,
Sulphate of magnesium	. . . . .	18.52     ,,
Nitrate of magnesium	. . . . .	5.64       ,,
Alkaline chlorides	. . . . .	79.85     ,,
Organic matter	. . . . .	.22       ,,
		<hr/>
		266.59

Total hardness	. . . . .	123.5 degrees.
Saline ammonia	. . . . .	0.007 grains per gallon.
Ammonia from organic matter		0.015       ,,
Nitrogen as nitrates, &c.	. . . . .	0.948       ,,

At the same time, Dr Letheby determined the sulphuric acid and chlorine in two samples of the vinegar in the store-vats at the works, and in a sample of Messrs Hill & Evans' vinegar purchased of a retail dealer at Bedford, and said to be adulterated. The following were the results obtained from the four samples in question:—

	Sulphuric Acid (SO <sub>3</sub> ).	Chlorine.
Water from the well at the works	97.14 grs. per gall.	48.44 grs. per gall.
A. Vinegar from store vats	90.79       ,,	50.33       ,,
B.       "       "	92.19       ,,	49.98       ,,
C. Vinegar from Bedford	91.70       ,,	49.42       ,,

merely decomposes the acetates naturally present in the vinegar, with liberation of acetic acid and formation of metallic sulphates or chlorides. Hence, only the *excess* of mineral acid beyond that required for the decomposition of the acetates, &c., can exist in the free state, and to the presence of such *free* mineral acid only can objection reasonably be taken.\*

Acetates and most other salts of organic acids, are decomposed by ignition into carbonates, which have an alkaline reaction, while sulphates and chlorides of the light metals are unchanged on ignition, and possess a neutral reaction. Hence, if the ash of a vinegar have a sensibly alkaline reaction, acetates must have been present in the original vinegar, and therefore no free sulphuric or hydrochloric acid can have been present. To determine the amount of free mineral acid, it is sufficient to carefully neutralise the vinegar with standard solution of soda before evaporation to dryness (the same process serves for a determination of the total free acid), ignite the residue, and titrate the aqueous solution of the ash with standard acid. If the free acid originally present were wholly organic, the ash will contain an equivalent amount of alkaline carbonate, which will require an amount of standard acid for its neutralisation exactly equivalent to the amount of standard alkali originally added to the vinegar. Any deficiency in the amount of standard acid required for neutralisation is due to the free mineral acid originally present in the vinegar. More accurate results are obtained if the amount of standard alkali added before evaporation is insufficient for the saturation of the acetic acid, but more than enough for the neutralisation of all mineral and fixed organic acids which may be present. By thus proceeding, decinormal alkali and acid may be employed (50 c.c. of the vinegar being used), and thus sharper readings obtained.†

The total chlorine, existing both as free hydrochloric acid

\* Unless the mineral acid used were contaminated with *arsenic*, as is frequently the case.

† This method was first suggested by Mr O. Hehner (*Analyst*, i. page 105).

and as metallic chlorides, cannot be determined in vinegar by direct precipitation with silver nitrate, other matters being thrown down simultaneously. For a correct determination, 50 c.c. of the vinegar should be neutralised with alkali, evaporated to dryness, the residue ignited, dissolved in water, and the aqueous solution precipitated with excess of calcium sulphate or nitrate to remove phosphates. The filtrate from this precipitate may be precipitated by, or titrated with, a solution of silver nitrate. The sulphuric acid and sulphates may be precipitated by the direct addition of barium chloride to the diluted vinegar, but the determination has little value.

Free sulphuric acid, as distinguished from sulphates, may be determined with considerable accuracy by evaporating 100 c.c. of the vinegar to a small bulk, and then adding to the cold concentrated liquid four or five times its bulk of alcohol. Sulphates are precipitated, while free sulphuric acid remains in solution. The filtered liquid is diluted, the alcohol boiled off, and the sulphuric acid precipitated with barium chloride. The precipitate is filtered off, washed, dried, ignited and weighed. Its weight multiplied by 0.4206 gives the weight of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) in the quantity of vinegar taken. In a vinegar free from chlorides, this process gives results in accordance with Hehner's process, but in their presence the mineral acid found is deficient by the amount of sulphuric acid required to decompose the chlorides. This difficulty may be obviated by treating the vinegar with excess of sulphate of silver solution before evaporation.\*

For the qualitative detection of mineral acids in vinegar, Strohl † utilises the insolubility of calcium oxalate in acetic acid and its solubility in presence of mineral acids. 1 c.c. of decinormal ammonium oxalate and an equivalent amount of calcium chloride solution are added to 50 c.c. of the vinegar

\* "Experiments on the determination of the free acids of vinegar," by Allen and Bodmer (*Analyst*, June 1878).

† *Journ. Chem. Soc.* 1877, i. 752. I have no experience of this method.



under examination. If the turbidity at first produced does not disappear on stirring, 1 litre of the sample contains less than

2.85 grammes of hydrochloric acid of 1.174 sp. gr., or

4.40 grammes of nitric acid of 1.330 sp. gr., or

1.70 grammes of sulphuric acid of 1.843 sp. gr.

Another method for separating and determining free mineral acids in vinegar is to neutralise a known quantity with quinine,\* evaporate the liquid to dryness, exhaust the residue with rectified spirit, and filter from the undissolved matter. The alcoholic liquid contains acetate of quinine, together with any sulphate, hydrochlorate, or nitrate of quinine which may have been formed from mineral acid originally present. On evaporating off the alcohol these acids may be detected and estimated in the usual way.

The detection of tartaric acid in vinegar has been described on page 196.

The presence of oxalic acid in vinegar may be detected by evaporating 20 c.c. to a small bulk, diluting with water, and adding calcium acetate solution, or a mixture of acetate of ammonium and chloride of calcium. Any oxalic acid causes the formation of white oxalate of calcium.

The detection of lead or copper may be effected as described on page 192.

Arsenic has been occasionally met with in vinegar, and may be introduced by the addition of impure hydrochloric or sulphuric acid. It may readily be detected by Marsh's or Reinsch's test.

Zinc is occasionally present in vinegar. It may be detected

\* The quinine for this purpose is best prepared by dissolving the commercial sulphate in dilute sulphuric acid, adding excess of ammonia, and shaking with ether. The ethereal solution of quinine is removed with a pipette, the ether distilled off by the heat of a water-bath, and the residual quinine dissolved in spirit. The solution thus obtained may be used for neutralising the vinegar. I have no experience of the quinine process for detecting mineral acids, and am ignorant of its author. The method appears very feasible, but the amount of quinine required would be considerable.



by boiling down the vinegar to dryness with nitric acid, dissolving the residue in acidulated water, passing sulphuretted hydrogen, filtering from any precipitate, and then adding ammonium acetate, when white sulphide of zinc will be thrown down if the metal be present.\* A less satisfactory method is to neutralise the greater part of the free acid in the original vinegar by ammonia, and then at once pass sulphuretted hydrogen.

Cayenne pepper, ginger, &c., are sometimes added to vinegar to confer pungency. They may be detected by neutralising the concentrated vinegar with sodium carbonate, and *tasting* the liquid.

Flies (*Musca cellaris*) and "Eels" (*Vibrio aceti*) are often found in vinegar. They are readily detected by the microscope, and may be destroyed by raising the liquid to 100° C.

**Metallic Acetates.**—Many of these important salts are extensively used in the arts, medicine, &c. Their analytical characters and the general methods adopted for their assay have been in great measure described already (see page 189, *et seq.*). The following observations, therefore, have reference chiefly to the detection of impurities and adulterations in commercial acetates.

**Aluminium Acetate.**  $Al'''(C_2H_3O_2)_3$ .—This salt is employed in solution by calico-printers, under the name of "red-liquor." It is usually prepared by precipitating a solution of alum or aluminium sulphate, by means of calcium or lead acetate, and filtering or syphoning off from the precipitated calcium or lead sulphate. When prepared by means of alum, the product necessarily contains sulphate of potassium or ammonium (according to the kind of alum used), and, as an excess of the precipitant should be avoided, aluminium sulphate is always to be expected. Owing to sulphate of calcium

\* In presence of iron, the white precipitate will be more or less discoloured and should be filtered off, dissolved in bromine water, the solution nearly neutralised, boiled with ammonium acetate, filtered, and sulphuretted hydrogen again passed through the filtrate.

being somewhat soluble in water, it will be met with in red-liquors prepared with acetate of calcium. Such red-liquor is inferior to that prepared by acetate of lead. The commercial article has a density of 1.087 to 1.100. Carbonate of sodium is often added to red-liquor to neutralise excess of acid.

**Ammonium Acetate.**  $(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_2$ .—This salt is generally met with in solution, but may be obtained in the solid state, when it is apt to contain acetamide,  $\text{C}_2\text{H}_3\text{O}, \text{H}_2\text{N}$ .

Ammonium acetate is liable to contain much the same impurities as the potassium salt, and may be examined in a similar manner (see page 210). It should be wholly volatile on ignition.

**Calcium Acetate.**  $\text{Ca}''(\text{C}_2\text{H}_3\text{O}_2)_2$ . This salt crystallises with difficulty in prismatic needles containing one atom of water. It is decomposed by heat into acetone,  $\text{C}_3\text{H}_6\text{O}$ , and calcium carbonate.

Calcium acetate should be completely soluble in water or in proof-spirit. An insoluble residue may consist of calcium sulphate, carbonate, &c. The solution should give no precipitate with argentic nitrate or barium chloride. Potassium ferrocyanide colours the solution blue if the sample contain iron, and brown if copper be present.

Acetate of calcium is obtained in the manufacture of acetic acid from crude pyroligneous acid. The commercial product is often extremely impure, containing much tarry matter, carbonate and sulphate of calcium, &c. On this account its assay is a matter of some commercial importance, and is not so easily effected as might appear at first sight. Thus, if the salt be ignited, and the amount of acetic acid calculated from the weight of the residual calcium carbonate, or from the amount of normal acid the residue will neutralise, very erroneous results may be obtained.\*

\* This is well shown by the following figures given by the late Mr William Baker. The results in column A were obtained by distilling the samples with

Another much used method of assaying crude acetate of calcium (pyrolignite of lime) is to boil the aqueous solution of the sample with a known amount of carbonate of sodium, and then to filter off the precipitated calcium carbonate. The loss of alkalinity found by titrating the filtered liquid represents the amount of acetic acid previously in combination with the lime. This rapid and valuable process is liable to give results above the truth, owing to the acid character of some of the tarry matters.

Fresenius has devised a method for the assay of crude acetate of calcium, the details of which are as follows:—5 grammes of the sample are dissolved in water, and mixed with 70 c.c. of normal oxalic acid. The liquid is then diluted with water to 250 c.c., and 2·1 c.c. extra water added to compensate for the space occupied by the precipitated calcium oxalate. The liquid is filtered, and 100 c.c. of the filtrate titrated with normal alkali. In another volume of 100 c.c., the excess of oxalic acid is precipitated with pure calcium acetate, and the precipitate filtered, washed, moistened with sulphuric acid, and weighed. The weight of  $\text{CaSO}_4$  so obtained, multiplied by ·9265, gives the amount of crystallised acetic acid in 100 c.c. of the solution (=2 grammes of the sample). By multiplying this result by ·9523 (or the weight of  $\text{CaSO}_4$  at once by ·882), the equivalent amount of acetic acid is obtained, and by subtracting this figure from the total acidity calculated as acetic acid (1 c.c. of normal  $\text{NaHO}$  = ·060 grammes  $\text{HC}_2\text{H}_3\text{O}_2$ ), the amount of actual acetic acid is found.

Calcium acetate may also be accurately assayed by the distillation process. For this purpose 5 grammes of the sample are dissolved in 50 c.c. of water, and 50 c.c. of phosphoric phosphoric acid, and titrating the distillate with standard alkali. The figures in column B were deduced from the weight of the ash of the sample.

		A.	B.
		By distillation.	By ignition.
No. 1.	Calcium acetate	70·17 per cent.	85·47
No. 2.	„ „	69·98 „	85·30
No. 3.	„ „	32·29 „	73·78

acid of 1·2 sp. gr. added. The phosphoric acid must be free from nitric acid. If either it or the sample contain chlorides, some sulphate of silver must be added. The liquid is placed in a small retort and distilled carefully to dryness, taking care to avoid spurting. The residue in the retort is treated with 50 c.c. of water, and the liquid again distilled to dryness. The process is again repeated, if necessary, until the distillate is no longer acid. The united distillates are made up with water to 250 c.c., and, after mixing, 50 c.c. are titrated with standard caustic alkali, using litmus or cupric sulphate as an indicator. Oxalic or sulphuric acid may be substituted for the phosphoric, but not with much advantage.

When *pure* calcium acetate is assayed by either of the above methods fairly accurate results may be obtained, but when commercial samples are examined, the errors sometimes become very serious. On the whole, the method of distillation with phosphoric acid is the most accurate, but unless very carefully performed, the results are liable to be considerably below the truth, from incomplete volatilisation of the acetic acid, while on the other hand, they may be excessive if nitric or other volatile acid be present in the phosphoric acid used.\*

\* The following results, obtained in my laboratory by the assay of the *same sample* of "acetate of lime" by different methods, show the nature and direction of the errors to which the various processes are liable.

	Acetic Acid. Per Cent.
By distillation with $\text{H}_3\text{PO}_4$ , and titration of distillate . . .	47·4
" " " " " " . . .	48·0
" " $\text{H}_2\text{SO}_4$ " " " " . . .	48·6
" " $\text{H}_2\text{C}_2\text{O}_4$ " " " " . . .	48·3
" " " " " " " " . . .	48·4
By Fresenius's method (see page 204) . . . . .	53·4
" " " " " " " " . . . . .	53·2
By ignition and weighing the $\text{CaCO}_3$ . . . . .	53·2
" and titration of residue . . . . .	53·2
" " " " " " " " . . . . .	53·8
" " " " " " " " . . . . .	54·0
By boiling with $\text{Na}_2\text{CO}_3$ , and titrating filtrate . . . . .	56·4
" " " " " " " " . . . . .	56·4
" " " " " " " " . . . . .	57·6



**Cupric Acetates.**—Several of these salts are known and extensively used in the arts. They are prepared by the action of acetic acid on oxide or carbonate of copper, or upon metallic copper, with free access of air. The neutral acetate is freely soluble in water, but several basic acetates exist. They are of various shades of colour, and constitute the bodies known as blue and green verdigris.

Good verdigris should be dry, soluble in dilute acetic or sulphuric acid, and also in ammonia. Verdigris is sometimes adulterated. Sand, clay, pumice, chalk, sulphates of barium, calcium and copper, and salts of iron and zinc are sometimes present.

On dissolving the sample in dilute hydrochloric acid, any sand, clay, pumice, or sulphate of barium will be left insoluble, and may be collected and weighed. (About 3 per cent. of insoluble matter is allowable in verdigris. If the residue amount to 6 per cent. the sample is inferior. Sulphate of calcium, if present in large proportion, may be left partially in the insoluble residue). If the sample effervesced in addition of acid, a carbonate is present, though it may be that of copper. From a measured portion of the solution in acid the sulphates may be precipitated by barium chloride, and the  $\text{BaSO}_4$  collected and weighed.

For the detection of the metals, the sample should be ignited, the residue dissolved in hydrochloric acid, and the copper precipitated from the diluted liquid by a current of sulphuretted hydrogen. In the filtrate, the excess of sulphuretted hydrogen is destroyed by bromine water, the liquid nearly neutralised by ammonia, and then boiled with ammonium acetate. The precipitate, when washed and ignited, leaves the iron as  $\text{Fe}_2\text{O}_3$ . The filtrate from the iron precipitate is treated with sulphuretted hydrogen, and any white sulphide of zinc filtered off, carefully roasted, and weighed as  $\text{ZnO}$ . From the filtrate the calcium is precipitated by ammonium oxalate. The precipitate yields calcium carbo-

nate on gentle ignition, the weight being equal to the chalk in the quantity of the sample taken. The calcium may be determined more readily, but less accurately, by dissolving the sample in hydrochloric acid, precipitating the iron by bromine and ammonia, and then at once treating the blue ammoniacal filtrate with ammonium oxalate. Of course, it does not follow that all the calcium found exists as chalk, unless sulphates are absent. The presence of zinc in verdigris is due to the use of sheets of brass instead of copper for corrosion by acetic acid.

**Iron Acetates.**—Both ferrous and ferric acetates are used in the arts. A crude variety of iron acetate is known as pyrolignite of iron.

For use by calico-printers, a liquid consisting chiefly of a solution of ferrous acetate, but always containing a little ferric acetate, is prepared by acting on scrap-iron by pyroligneous acid of 1.035 to 1.040 specific gravity. The product has a density of 1.085 to 1.090, and is concentrated by boiling till the density is about 1.120, when it contains about 10 per cent. of iron. It is then ready for use, and is known as "printers' iron liquor." For use by dyers, the liquid is not concentrated by evaporation, but the density is raised by the addition of ferrous sulphate (copperas), by which a more suitable product is said to be obtained than is yielded by acetate of iron alone. As a 5 per cent. solution of crystallised ferrous sulphate has a density of 1.026, the addition of  $\frac{1}{2}$  lb. of copperas to the gallon of "black liquor" will raise its density from 1.085 to 1.111. Sulphate of iron may be detected and estimated by precipitating the diluted black liquor with barium chloride. 233 parts of the precipitate represent 278 parts of crystallised ferrous sulphate. Black liquor is frequently adulterated with common salt, a 5 per cent. solution of which has a density of 1.036. It may be detected and estimated by adding nitric acid and precipitating the diluted liquor with nitrate of silver.

FERROUS ACETATE is occasionally made by decomposing

a solution of ferrous sulphate by calcium acetate. The liquor has usually a density of 1.11, and contains calcium sulphate.

FERRIC ACETATE is sometimes preferred by dyers and printers to the ferrous salt. It is occasionally prepared by decomposing iron-alum or ferric sulphate by lead acetate. The product must be free from excess of the lead salt, and, for some purposes, excess of ferric sulphate must be avoided.

TINCTURE OF ACETATE OF IRON is used in medicine. It is prepared by mixing alcoholic solutions of potassium acetate and ferric sulphate, and filtering from the precipitated sulphate of potassium.

**Lead Acetates.**—These important salts include the neutral acetate,  $\text{Pb}''(\text{C}_2\text{H}_3\text{O}_2)_2$ , often called "sugar of lead," and no fewer than four basic- or oxy-acetates, all of which are more or less soluble in water, the solutions possessing an alkaline reaction and giving a precipitate of lead carbonate by the action of carbonic acid gas.\* All the basic acetates may be considered as compounds of the neutral acetate with oxide or hydrate of lead. By suspending the sample in water, and passing carbonic acid through the liquid as long as it has an alkaline reaction, the oxide of lead is separated as an insoluble carbonate, and may be filtered off, washed, ignited in porcelain (apart from the filter) till bright-yellow when cold, and weighed as  $\text{PbO}$ .

The lead remaining in permanent solution exists as neutral acetate, and may be determined by precipitation as sulphate or chromate. A better and simpler method for detecting basic acetate in a sample is to dissolve it in recently-boiled water, filter, and then add to the clear solution an equal measure of a 1 per cent. solution of mercuric chloride. A white precipitate proves the presence of basic acetate.† The assay may

\* A solution of neutral lead acetate is slightly precipitated by carbonic acid.

† Besides their reactions with mercuric chloride, carbonic acid, and litmus, the basic acetates of lead are distinguished from the neutral acetate by their property of being precipitated by a strong solution of nitre added in excess. The precipitate appears to be ortho-nitrate of lead,  $\text{Pb}_3''(\text{NO}_4)''_2$ .



also be conducted by methods 4, 5, or 7 (pages 190 and 191).

R. Fresenius recommends the following indirect method for the assay of pyrolignite and acetate of lead :—10 grammes of the sample are dissolved in water in a flask holding 500 c.c., 60 c.c. of normal sulphuric acid are added, and then water up to the mark. An extra 1·3 c.c. of water is added to compensate for the bulk of the precipitated lead sulphate. The flask is closed, well shaken, and the liquid allowed to settle. 100 c.c. of the clear liquid are taken out, precipitated with barium chloride, and the resultant  $\text{BaSO}_4$  collected, washed, ignited, and weighed. Its weight, multiplied by ·4206, is subtracted from ·588 grammes (the weight of  $\text{H}_2\text{SO}_4$  added to each 100 c.c. of the liquid). The remainder, multiplied by 113·7, gives the percentage of  $\text{PbO}$  in the sample. Another 100 c.c. of the clear liquid are drawn off and titrated with normal soda solution, using litmus as an indicator. Multiply the number of c.c. of alkali used by ·060, subtract from this the previously obtained weight of  $\text{BaSO}_4$  multiplied by ·515 (=the free sulphuric acid expressed in terms of acetic acid), and the remainder, multiplied by 50, will be the percentage of acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ) in the sample.

SOLUTION OF OXY-ACETATE OF LEAD is an official remedy. It is described in the British Pharmacopœia as a dense, colourless liquid, with alkaline reaction and sweet astringent taste, becoming turbid on exposure to air; forming, with mucilage of gum arabic, a white opaque jelly; the density is 1·26. A dilute solution is officially prepared by mixing the above with an equal measure of alcohol, and then adding enough water to make up 80 times the original measure. Solution of oxy-acetate of lead is prepared by boiling 10 parts of neutral acetate with 7 of finely-powdered litharge and 40 of water. After half an hour, the liquid is filtered and made up to the original bulk with water.

**Potassium Acetate.**  $\text{KC}_2\text{H}_3\text{O}_2$ .—This salt exists in



several vegetable secretions. It is deliquescent, very soluble in water and alcohol, and in solution is neutral to test-paper. It undergoes fusion when heated to incipient redness, and at a higher temperature decomposes and leaves a residue of potassium carbonate. The amount of acetate present in commercial samples of the salt may be determined by the general methods given on page 190, *et seq.*

COMMERCIAL ACETATE OF POTASSIUM is liable to contain sulphates, chlorides, and carbonates; also salts of iron, lead, copper, and zinc; arsenic is occasionally present. It is sometimes intentionally adulterated, acetate of calcium, and sulphate, tartrate, and carbonate of potassium being employed for the purpose.

Acetate of potassium being readily soluble in rectified spirit, any admixture of sulphates, tartrates, or carbonates may be detected and estimated by treatment with that solvent. Carbonate is indicated more precisely by the alkaline reaction of the sample, its precipitation by chloride of calcium, its power of decolorising iodised starch, and by the effervescence produced on adding an acid.

**Sodium Acetate**,  $\text{NaC}_2\text{H}_3\text{O}_2$ , closely resembles the potassium salt, but crystallises with three atoms of water. It is liable to contain the same foreign matters as the acetate of potassium. Crude sodium acetate often contains tarry matters derived from the pyroligneous acid employed in its preparation. Sodium acetate has been used for preserving meat.

## HOMOLOGUES OF ACETIC ACID.

Acetic acid is the most important and best known of the homologous series called "the fatty acids." These acids have the general formula  $\text{C}_n\text{H}_{2n}\text{O}_2$  or  $\text{C}_n\text{H}_{2n-1}\text{O}_2\text{OH}$ . The lower members of the series are volatile liquids closely resembling acetic acid. The higher members of the series are insoluble in water, not volatile without decomposition, and solid at ordinary temperatures. The fatty acid series is known up

to an acid containing 30 atoms of carbon, but the greater number of the members are of very limited importance, and their properties are insufficiently studied to admit of their analytical detection by reagents. The higher members of the series will be more conveniently considered in a section on "oils and fats,"\* and therefore this article is limited to a consideration of the analytical characters of the lower members of the series. These are,—

No. of C. Atoms.	Name of Acid.	Formula.	Boiling Point. °C.	Specific Gravity.	Solubility in Water.
1	Formic . .	$\text{H.CHO.O} = \text{H.COOH}$	100	1.235	Miscible in all proportions.
2	Acetic . .	$\text{H.C}_2\text{H}_3\text{O.O} = \text{CH}_3\text{.COOH}$	119	1.055	Do.
3	Propionic . .	$\text{H.C}_3\text{H}_5\text{O.O} = \text{C}_2\text{H}_5\text{.COOH}$	140	.9961 at 19°	Do.†
4	Butyric (normal)	$\text{H.C}_4\text{H}_7\text{O.O} = \text{C}_3\text{H}_7\text{.COOH}$	163	.9817 at 0° .958 at 14°	Do.
"	Iso-butyric . .	" " $= \text{C}(\text{CH}_3)_2\text{H.COOH}$	154	.9598 at 0° .9503 at 20°	Soluble.
5	Valeric (normal)	$\text{H.C}_5\text{H}_9\text{O.O} = \text{C}_4\text{H}_9\text{.COOH}$	185	.9577 at 0° .9415 at 20°	{ Sparingly soluble. (1 in 30)
"	Iso-valeric . .	" " $= \text{C}_2(\text{CH}_3)_2\text{H}_3\text{.COOH}$	175	.937 at 15°	Do.
"	Hydrate of Iso-valeric	$\text{H.C}_5\text{H}_9\text{O.O} + \text{H}_2\text{O}$	165	.950 at 15°	Do.
"	Trimethyl-acetic	$\text{H.C}_5\text{H}_9\text{O.O} = \text{C}(\text{CH}_3)_3\text{.COOH}$	161	...	Do. (1 in 40)
6	Caproic (normal)	$\text{H.C}_6\text{H}_{11}\text{O.O} = \text{C}_5\text{H}_{11}\text{.COOH}$	205	.931 at 15°	Nearly insoluble.
"	Iso-caproic . .	" " $= \text{C}_3(\text{CH}_3)_2\text{H}_5\text{.COOH}$	199-200	.931 at 0°	Do.
7	{ Enanthylic } (normal)	$\text{H.C}_7\text{H}_{13}\text{O.O} = \text{C}_6\text{H}_{13}\text{.COOH}$	223	...	Almost insoluble.
8	Caprylic . .	$\text{H.C}_8\text{H}_{15}\text{O.O}$	234-238	...	Insoluble.
9	Pelargonic . .	$\text{H.C}_9\text{H}_{17}\text{O.O}$	253-254	...	Do.
10	Capric or Ruric	$\text{H.C}_{10}\text{H}_{19}\text{O.O}$	268-270	...	Do.

It will be seen from this table that all the acids, except the first three, are capable of isomeric modification.† In the case of enanthylic, caprylic, pelargonic, and capric acids, these isomeric modifications are unknown, or are of too little importance to require special notice. As a rule, the various isomeric modifications of any particular acid present few tangible differences, except in the density and boiling point. Hence their analytical characters are practically identical, though further research will probably prove the existence of greater differences than are now suspected.

\* This section is not included in the present volume, as fats are not connected with the subjects dealt with at present, except in their chemical relationships.

† See page 222.

‡ Respecting an isomeric modification of propionic acid, see page 223.

As we ascend the series, the members of it diminish in density, volatility, and solubility in water, while their melting points rise. Among the normal members of the series, the boiling points differ very constantly by 18 to 22° C., for each increment of  $\text{CH}_2$  added to the formula. The iso-modifications generally have lower boiling points than the corresponding normal acids.

Comparatively few of the homologues of acetic acid require separate consideration in detail. The separation of the various members of the series from each other cannot usually be effected very readily or perfectly, the most satisfactory methods being based on the following principles:—

*a.* The lowest members of the series are the most readily soluble in aqueous liquids. All but formic, acetic, and propionic\* acids are separated from their aqueous solutions by saturating the liquid with calcium chloride, when they rise in the form of oils. A more perfect separation from acetic and formic acids of the acids higher than valeric may be effected by shaking the acidulated aqueous solution with ether, which dissolves the higher homologues.

*b.* The lower members of the series are most chemically active. Hence, if an amount of alkali insufficient for complete neutralisation be added to a solution containing the free acids, and the liquid be then distilled, the higher members of the series pass over in the free state, while the lower members remain behind as fixed salts. Butyric and iso-valeric acids exhibit an exception to this principle, iso-valeric acid completely decomposing butyrates.

*c.* A most ingenious method of detecting other fatty acids in presence of acetic acid, and estimating the proportions present, has been described by M. Duclaux.† It is based primarily on the curious fact that if a liquid containing any fatty acid be distilled, each successive fraction of the distillate

\* The statements respecting the solubility of propionic acid are conflicting. See page 222.

† *Ann. Chim. Phys.* [5] ii. pp. 233–289.

contains a proportion of the total acid operated on which is practically constant for the same fraction, but will vary according to the nature of the acid employed. Thus, M. Duclaux found that if 110 c.c. of a liquid containing acetic acid were distilled in a retort of 250 to 300 c.c. capacity, each succeeding 10 c.c. of distillate contained an increasing quantity of acid, which amounted to 79.8 per cent. of the whole when 100 c.c. had passed over. Each of the homologues of acetic acid has a special rate of vaporisation, and it is a curious fact that the less volatile acids pass over with the first portions of aqueous vapour, while acetic and formic acids behave in an opposite manner.

The presence of foreign matters has a sensible, but not very serious, effect on the rate of distillation. Alcohol diminishes the proportion of acid in the first portions of the distillate, but by the time  $\frac{1}{11}$ ths has distilled, the proportion of acid in the receiver is the same as in the absence of alcohol. Glycerin diminishes slightly the proportion of acid volatilised, doubtless owing to the formation of a glycylic ether, but the effect can be destroyed by adding tartaric acid to the contents of the retort.

The author has no personal experience of Duclaux's process, beyond an attempt to apply it to the assay of commercial "acetate of lime" (page 203). The salt was dissolved in water, oxalic acid added, and the calcium oxalate filtered off. On distilling the filtrate to  $\frac{1}{11}$ , a tolerably constant proportion of acetic acid passed over, but it was considerably below 79.8 per cent. of the total quantity present in the sample.

The following table gives M. Duclaux's results in a concise form. The columns headed B. show the percentages of the total acid contained in each successive 10 c.c. of distillate, when 110 c.c. of the liquid were distilled in a retort holding 250 to 300 c.c. The columns headed A. show the percentages of the total distilled acid which passed over in each 10 c.c. when the 100 c.c. first obtained was redistilled. The determinations of acid in the distillate were made by standard lime water:—



	Percentage of Total Acid contained.									
	Formic.		Acetic.		Propionic.		Butyric.		Valeric.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
1st fraction of 10 c.c. .	Per cent. 5.5	Per cent. 3.5	Per cent. 7.5	Per cent. 5.9	Per cent. 11.3	Per cent. 10.5	Per cent. 16.8	Per cent. 16.4	Per cent.	24.5
2d " " .	6.4	4.1	7.9	6.2	11.5	10.6	15.1	14.7		20.0
3d " " .	6.6	4.2	8.2	6.7	11.2	10.4	13.5	13.2		15.4
4th " " .	7.2	4.5	8.6	6.9	10.6	9.9	12.3	11.8		11.4
5th " " .	8.3	5.3	9.1	7.3	10.7	9.9	10.2	10.1		8.2
6th " " .	9.1	5.7	9.6	7.6	10.1	9.3	9.3	9.1		6.2
7th " " .	10.0	6.4	10.2	8.2	9.3	8.9	7.8	7.6		4.0
8th " " .	12.1	6.7	11.5	9.2	9.3	8.5	6.4	6.3		3.1
9th " " .	14.6	9.3	12.4	9.8	8.5	7.8	5.0	4.8		2.6
10th " " .	20.2	12.8	15.1	12.1	7.5	7.0	3.6	3.5		1.5
Total distillate=100 c.c.	100.0	63.5	100.0	79.8	100.0	92.8	100.0	97.5		96.9
Remaining in retort= 10 c.c. }	...	36.5	...	20.2	...	7.2	...	2.5		3.1

It appears from this table that when a solution of acetic or formic acid is distilled, the first portions which come over are very weak, and that the strength of the distillate rises regularly till the end of the operation. On the other hand, propionic, butyric, and valeric acids come over chiefly at the commencement of the process.

When two or more of these acids are present together in a liquid, each maintains its own characteristics when the distillation is carried out as described. Hence, not merely the nature, but the quantities of the acids present may be ascertained by calculation—at least in certain cases. Thus, suppose the numbers obtained for the "B" column by the distillation of a certain liquid to have been as follow:—8.6, 8.7, 8.7, 8.7, 8.8, 8.7, 8.9, 9.1, 9.7, 10.3 per cent. These results may safely be presumed to be produced by a mixture of acetic acid with either butyric or propionic acid. Assume the mixture to consist, of  $a$  equivalents of acetic and  $p$  equivalents of propionic acid; then, by the table, we have for the 1st fraction of 10 c.c.—

$$8.6(a+p) = 5.9a + 10.5p$$

$$\therefore p = 1.2a.$$

Proceeding in the same way with the percentages of acid found in the succeeding fractions of distillate, we obtain the following series of numbers:—1.1, 1.0, 1.0, 1.0, 1.0, 1.0, 1.0, 1.0, 1.1. Hence the amount of propionic acid is the same, or

slightly in excess, in equivalents, of the acetic. For various reasons, the inferences to be drawn from the first and last fractions are the least trustworthy. But suppose the mixture were one of acetic and butyric acids; then,

$$8.6(a+b)=5.9a+16.4b$$

$$\therefore b=3.2.$$

Proceeding in the same way with the other fractions, we obtain the following series of numbers:—3.1, 3.0, 2.8, 2.5, 2.5, 2.2, 2.1, 1.6, 1.3. Thus we have ten estimations of the butyric acid, in which its equivalent amount varies from 3.2 to 1.3 times the acetic acid present. The variation in these determinations renders the assumption of the second acid being butyric acid absurd. Hence, the two acids were acetic and propionic in about equivalent proportions.

In the original paper, M. Duclaux gives a number of tables which materially facilitate calculation.

In applying the method to the examination of wines, Duclaux recommends the following mode of procedure:—

275 c.c. (=25 × 11), or a multiple of this quantity, are shaken, and a current of air passed through the liquid, in order to remove carbon dioxide. The wine is then distilled till 250 c.c. have passed over, and the distillate, after again drawing air through it, is titrated with standard lime water. An excess of the latter is then added, and the liquid is evaporated to about 250 c.c., in order to volatilise the alcohol. A gramme of glycerin is then added, and sufficient tartaric acid to set all the volatile acids at liberty. The calcium tartrate is allowed to crystallise, and is then separated from the liquor, the volume of which is again brought to 275 c.c. About 1 gramme of tartaric acid is now added, and the liquid distilled till 250 c.c. have passed over, when the whole distillate is again titrated. The lime water now required will bear the same proportion to that used for the first titration, that the amount of volatile acid indicated by the first titration bears to the total quantity present in the wine. The titrated liquid is

now brought to 165 c.c., and 150 c.c. distilled over, after adding an amount of tartaric acid exactly equivalent to the lime water used in the titration. 50 c.c. of the distillate are titrated, while the remainder is diluted to 110 c.c., and 100 c.c. distilled over, each fraction of 10 c.c. being separately titrated. The numbers thus obtained give the necessary data for ascertaining the nature and amount of the volatile acids present.\* The following example indicates the mode of calculation. 275 c.c. of wine were taken and distilled to  $\frac{1}{11}$ . 250 c.c. of distillate required 316 c.c. of lime water. On adding tartaric acid and distilling over  $\frac{1}{11}$ , the distillate required 263 c.c. of lime water. Hence 83.3 per cent. of the total acid passed over on distilling to  $\frac{1}{11}$ , and, assuming the same proportion in the first distillation, the free acid in the original wine would have required  $\frac{316}{263}$  of 316 = 379 c.c. of lime water for its neutralisation.

On referring to the table on page 214, it will be seen that when a liquid containing acetic acid is distilled to  $\frac{1}{11}$  of its bulk, about 80 per cent. of the acid passes over, while 93 per cent. of the propionic acid distils under similar circumstances. On repeating the process, 80 and 93 per cent. of *these* amounts will be respectively obtained. Hence the third and last dis-

\* In the above process, I think standard baryta water might be advantageously substituted for the lime water, and standard sulphuric acid for the tartaric acid recommended (except where about 1 gramme of tartaric acid is directed to be added to represent the acidity of the original wine). This modification would allow the sulphate of barium to be filtered off immediately, instead of having to wait for the calcium tartrate to crystallise. In the last titrations, the use of baryta water would cause the acids to be obtained in the form of barium salts, which could be dried at 130° C., weighed, and converted into BaSO<sub>4</sub>, as described in method *d*, page 217. A very useful check would thus be obtained.

From some recent experiments of M. Duclaux (*Ann. Chim. Phys.* [5], xiii. 86), it also appears very probable that higher volatile fatty acids might be detected and approximately estimated in presence of acetic acid by observing the number of drops of the liquid delivered by a pipette constructed to give 100 of water. The higher the acid in the series, the less the surface tension and the greater the number of drops formed.

tillate will contain  $\frac{80 \times 80 \times 80}{100 \times 100 \times 100} = \frac{512}{1000} = 51.2$  per cent. of

the total acetic acid present in the wine, and  $\frac{93 \times 93 \times 93}{100 \times 100 \times 100} =$

80.4 per cent. of the total propionic acid. Thus, if the titration of the fractions obtained in the third distillation showed acetic and propionic acid to be present in equivalent proportions, the equivalent amounts of these acids present in the original wine would be as 80.4 to 51.2, or as 100 equivalents of acetic to 63.7 of propionic acid. Thus of 379 c.c. of lime water, required by the volatile acids in 275 c.c. of the original wine,  $\frac{100}{164}$  of that quantity, or 231 c.c., were neutralised by acetic

acid, and the remaining 148 c.c. by propionic acid. From the strength of the lime water and the atomic weights of acetic and propionic acids, the actual amounts of fatty acids present can be readily calculated.

By the above method, Duclaux proved the presence of valeric acid in perspiration, and of butyric acid in bread. He also found that the presence of butyric acid was characteristic of wine suffering from "bitterness," and propionic acid of wine in which the fermentation had been "pushed" too far.

The largest quantity of valeric acid found in wine by Duclaux was .006 grammes per litre. For its discovery, 7 or 8 litres must be distilled as already described, the distillate neutralised with lime, and then  $\frac{1}{40}$  of the sulphuric acid necessary to decompose the calcium salts added. On redistillation, the whole of the valeric acid passes over, while 39 equivalents out of every 40 of the fatty acids present remain in the retort.

*d.* Another method of detecting and determining fatty acids when in admixture with each other is as follows:—The free acids obtained by distillation are saturated by carbonate of barium, or by the cautious addition of baryta water (the latter method being preferable for the higher members of the series). In this way, neutral barium salts are formed, which may be



obtained in the anhydrous state by evaporating off the water and drying the residue at  $130^{\circ}\text{C}$ . These barium salts contain percentages of barium dependent on the atomic weights of the fatty acids present. On moistening the residue with sulphuric acid and igniting, an amount of barium sulphate is obtained proportional to the percentage of barium contained in the salt of the fatty acid present. The following table shows the proportions of Ba contained in, and of  $\text{BaSO}_4$  producible from, the barium salts of the lower acids of the acetic series :—

Name of Salt.	Formula of Salt.	Ba, per Cent.	$\text{BaSO}_4$ , per Cent.
Barium formate . .	$\text{Ba}_2\text{2CHO}_2$	70·25	119·47
„ acetate . .	$\text{Ba}_2\text{2C}_2\text{H}_3\text{O}_2$	53·73	91·37
„ propionate . .	$\text{Ba}_2\text{2C}_3\text{H}_5\text{O}_2$	48·41	82·13
„ butyrate . .	$\text{Ba}_2\text{2C}_4\text{H}_7\text{O}_2$	44·05	74·91
„ valerate . .	$\text{Ba}_2\text{2C}_5\text{H}_9\text{O}_2$	40·41	68·73
„ caproate . .	$\text{Ba}_2\text{2C}_6\text{H}_{11}\text{O}_2$	37·33	63·48
„ cenanthylate . .	$\text{Ba}_2\text{2C}_7\text{H}_{13}\text{O}_2$	34·68	58·98
„ caprylate . .	$\text{Ba}_2\text{2C}_8\text{H}_{15}\text{O}_2$	32·39	55·08
„ pelargonate . .	$\text{Ba}_2\text{2C}_9\text{H}_{17}\text{O}_2$	30·38	51·66
„ caprate . .	$\text{Ba}_2\text{2C}_{10}\text{H}_{19}\text{O}_2$	28·60	48·64

From this table it will be seen that the pure barium salts of the lower acids of the acetic series can very readily be distinguished from each other by estimating the percentage of barium contained in them. In the case of mixtures of two acids, the identity of which is established, the proportions in which the two are present may be calculated from the following formula, in which  $x$  is the percentage of barium salt of the lower fatty acid in the mixed barium salts obtained ; P, the percentage of  $\text{BaSO}_4$  yielded by the mixed barium salts on treatment with sulphuric acid ; B, the percentage of  $\text{BaSO}_4$  theoretically obtainable from the pure salt of the lower fatty acid ; and  $b$ , the percentage of  $\text{BaSO}_4$  theoretically obtainable from the pure salt of the higher fatty acid. Then :—

$$Bx = 100P + bx - 100b.$$

For example :—suppose a mixed barium salt known or assumed to consist of acetate and valerate yields 78·45 per

cent. of  $\text{BaSO}_4$  when treated with sulphuric acid and ignited. Then, by the above formula,—

$$\begin{aligned} 91.37x &= 7845 + 68.73x - 6873 \\ \therefore 22.64x &= 972 \\ \text{and } x &= 42.93. \end{aligned}$$

Hence, the mixed barium salt consisted of 42.93 of barium acetate, and 57.07 of barium valerate. From these data, and the weight of mixed barium salt found, the actual amounts of acetic and valeric acid may be readily calculated.

The above method has been proposed by A. Dupré\* for approximately determining the fusel oil in spirits. In this case, the various alcohols are converted into the corresponding acids by oxidation (see page 122). The ethylic alcohol yields acetic acid, while the higher homologues contained in fusel oil yield butyric, valeric, and still higher acids. They are assumed to be wholly valeric acid, and from the amount of the latter (deduced from the composition of the mixed barium salts) the corresponding amylic alcohol is calculated by multiplying by the factor .863.

c. An approximate separation of the homologues higher than valeric acid can be effected by a fractional crystallisation of their barium salts. The following is the order in which the barium salts are deposited :†—

From Aqueous Solutions.	From Alcoholic Solutions.
1. Barium caprate.	1. Barium caprylate.
2. „ pelargonate.	2. „ cœnanthylate.
3. „ caprylate.	3. „ pelargonate and
4. „ cœnanthylate.	caprate.
5. „ caproate.	4. „ caproate.

The aqueous or alcoholic solution of the acid is neutralised with standard aqueous or alcoholic solution of potash (accord-

\* *Analyst*, vol. i. p. 4.

† It is very probable that this method would be much affected by a change in the modifications of the acids. The normal and iso-varieties of the higher fatty acids are not at present thoroughly differentiated.

ing as the crystallisation is to be effected from an aqueous or an alcoholic solution), an amount of barium chloride equivalent to the potash is next added, and the resultant liquid evaporated, and allowed to deposit crystals. The crops of crystals from an aqueous solution may be washed with hot alcohol, the washings containing the salts in the reverse order of their deposition from alcoholic solution.

As a class, the lower members of the acetic acid series may be separated from most other organic acids (except lactic acid), by treating the aqueous solution with finely-ground oxide of lead, in quantity sufficient to render it slightly alkaline. On filtering, the lead salts of most organic acids will be left insoluble, while those of the acetic series will be found in the filtrate.

Of the homologues of acetic acid, only formic, butyric, propionic, and valeric acids are of sufficient importance to require separate consideration.

**Formic Acid.**  $\text{CH}_2\text{O}_2 = \text{H}, \text{CHO}_2 = \begin{matrix} \text{CHO} \\ \text{H} \end{matrix} \} \text{O} = \begin{Bmatrix} \text{H} \\ \text{CO.OH} \end{Bmatrix}$ .

—In general properties, formic acid strongly resembles acetic acid, but it is stronger in its chemical affinities, and more readily oxidised. Formic acid is contained in the liquid obtained by distilling ants with water. It is usually prepared by distilling oxalic acid with glycerin. It also results from the decomposition of chloroform or chloral by an alkali, and by the reaction of cyanogen gas or cyanides with water.

Formic acid is a colourless volatile liquid, of extremely irritating pungent odour. It is very acid, and, when concentrated, produces intense irritation on the skin.

The formates are all soluble in water. A neutral solution of a formate of alkali-metal gives the following reactions:—

1. Nitrate of silver gives, in concentrated solutions, white crystalline argentic formate,  $\text{AgCHO}_2$ , which darkens on standing, and is reduced to metallic silver when warmed. If the liquid be too dilute to allow of a precipitate being

formed, the reduction to metallic silver still occurs on heating. In presence of ammonia the reduction is retarded or prevented.

2. Mercuric chloride is reduced on heating, with production of white mercurous chloride, or grey metallic mercury, according to the proportion of formate present. Acetates do not give this reaction, but acetates and chlorides of alkali-metals retard or prevent the reduction. The reduction of formate of mercury on heating may be applied to the estimation of formic acid, and its separation from acetic acid may be approximately effected by boiling the solution of the free acids with *yellow* mercuric oxide until effervescence ceases. If formic acid only be present, the filtered liquid will be free from mercury. With a mixture of the two acids, the amount of mercury which passes into solution is equivalent to the acetic acid present. If the total acid present originally be determined by standard alkali or other means, the quantity of formic acid may be found. Or, in presence of other acids forming soluble mercuric salts, the excess of mercuric oxide may be dissolved by dilute hydrochloric acid, and the residual metallic mercury weighed, and calculated to formic acid.

$$\text{HgO} + \text{CH}_2\text{O}_2 = \text{Hg} + \text{CO}_2 + \text{H}_2\text{O}.$$

3. Chlorine, bromine, chromic acid, permanganate, and other powerful oxidising agents convert formic acid more or less readily into carbonic acid.

4. When heated gently with alcohol and sulphuric acid, formates generate ethyl formate,  $\text{C}_2\text{H}_5\text{CHO}_2$ , having a fragrant odour of peach-kernels, and boiling, when purified, at about  $55^\circ \text{C}$ .

5. With ferric chloride, formates react similarly to acetates. (See test 5, page 189).

6. At a gentle heat, strong sulphuric acid evolves carbon monoxide from formic acid or a formate. Strong alkalis produce an oxalate.

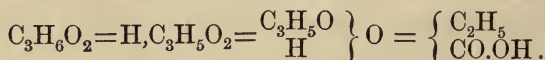
7. Formates of lead and magnesium are insoluble in alcohol.



The corresponding acetates are soluble. Hence, acetic may be separated from formic acid by saturating the free acids with a slight excess of calcined magnesia or carbonate of lead, filtering, evaporating the filtrate to a small bulk, and adding a large proportion of alcohol. Formate of magnesium or lead is precipitated, while the corresponding acetate remains in solution. The process may be varied by precipitating the alcoholic solution of the acids with an alcoholic solution of lead acetate, and washing the resultant precipitate with alcohol.

In addition to the methods already indicated, formic acid may be determined by titration with standard alkali, or by decomposition in a carbonic acid apparatus by sulphuric acid and bichromate of potassium, the amount of it being deduced from the weight of dry  $\text{CO}_2$  evolved.

**Propionic Acid.** Metacetic acid.



This acid is of no commercial importance, but its detection and separation from its homologues are occasionally necessary.

Propionic acid is contained in crude oil of amber, in sour cocoa-nut milk, and in certain wines, especially when the fermentation has been pushed too far. It is also produced by the fermentation of glycerin, and by a great variety of synthetic methods.

Propionic acid closely resembles acetic acid, but has a distinctly different smell.

The statements respecting the solubility of propionic acid are very conflicting. According to some observers, it is not miscible in all proportions with water, but floats as an oil on its saturated aqueous solution; according to others, it is not separated from its aqueous solution by a saturated solution of calcium chloride.

It is probable that these conflicting statements are due to

the existence of an isomeric modification of propionic acid, somewhat analogous to isobutyric acid.\*

The propionates closely resemble the acetates.

The following method is described by Linnemann for the separation of propionic acid from its lower homologues:—The free acids are evaporated to dryness with excess of litharge. The residue is then treated with cold water, and the liquid filtered. Basic propionate of lead dissolves, while any acrylate remains insoluble, together with most of the acetate and formate. The solution is boiled and stirred quickly, when the propionate separates suddenly and almost completely, and may be filtered off from the acetate and formate. The propionic acid of fermentation is said not to exhibit this reaction.

For other methods of detecting and separating propionic acid, see process *c.* page 212.

**Butric Acid.**  $C_4H_8O_2 = H, C_4H_7O_2 = \begin{matrix} C_4H_7O \\ H \end{matrix} \} O$ .—Two isomeric modifications of this acid are known, differing slightly in their physical properties (see page 211). Both kinds are colourless, mobile liquids, having a smell resembling, at the same time, acetic acid and rancid butter. Isobutyric acid has a much less offensive smell than the normal acid obtained by the decomposition of butter, or by the butyric fermentation of sugar.

Butyric acid exists ready formed in various natural products, and is a frequent result of the decomposition of animal and vegetable matter.

Butyric acid is soluble in water, alcohol, and ether in all proportions, but is not soluble in concentrated solution of calcium chloride or common salt; hence, it may be separated from its aqueous solution by saturating the liquid with calcium chloride, and then agitating with ether. From the ethereal

\* Butyracetic acid presents a very close analogy to propionic acid, both in the free state and in combination. It has also the same composition and boiling point as propionic acid.

layer it may be recovered by spontaneous evaporation, or, as a salt, by agitation with excess of solution of potash or soda.

For other methods of approximately separating butyric from acetic and valeric acids see pages 212 and 226.

All the metallic butyrates are soluble in water. Butyrate of lead is a heavy liquid, which solidifies when cooled.

Butyrate of copper forms bluish-green monoclinic crystals, which are sparingly soluble in water. The formation of cupric butyrate may be employed to distinguish butyric from valeric acid. See page 226.

The most delicate and characteristic reaction of butyric acid or a butyrate is the formation of ethyl butyrate on heating with alcohol and strong sulphuric acid. The ether has a most fragrant odour of pine-apples, and boils at  $119^{\circ}$  C. See pages 140 and 147.

**Valeric Acid.** Valerianic acid. Delphinic acid. Phocinic acid.  $C_5H_{10}O_2 = H, C_5H_9O_2 = \left. \begin{matrix} C_5H_9O \\ H \end{matrix} \right\} O$ .—Several varieties of valeric acid are known, as indicated by the formulæ in the table on page 211. They present close chemical resemblances, but differ somewhat in their physical properties, *e.g.*, their boiling points, and action on polarised light. Ordinary valeric acid ought in strict accuracy to be called iso-valeric acid. It is to this variety of valeric acid that the following descriptions apply.

Valeric acid occurs ready formed in valerian root, and in many plants of the natural order *Compositæ*; also in various secretions and products of animals.

Valeric acid is an unpleasant smelling, colourless, oily liquid; it has a sharp, acid taste, and bleaches the tongue. Valeric acid dissolves in about 30 parts of cold water, and is readily soluble in alcohol, ether, chloroform, or strong acetic acid; it is almost wholly removed from its aqueous solution by saturating the liquid with chloride of calcium or sodium.

Absolute valeric acid,  $C_5H_{10}O_2$ , has a density of .937 at

15° C., and boils at 175° C. With water it forms a hydrate of the composition  $C_5H_{10}O_2 \cdot H_2O$ , which has a density of .950 and boils at 165° C., but is gradually dehydrated by distillation, the weaker acid coming off first.

The presence of alcohol, acetic acid, valerates, &c., in commercial valeric acid is indicated by the increased solubility of the sample, which should not be greater than 1 of the hydrated acid in 26 parts by weight of water. If the sample require more than 30 parts of cold water for solution, the presence of higher homologues, or valeral (valeric aldehyde,  $C_5H_{10}O$ ) is indicated. By neutralising the sample with an alkali, any amylic alcohol, valeric aldehyde, or neutral ethers will be left undissolved, and their amount may be estimated by measurement, or the mixture may be shaken with ether, and the ethereal liquid evaporated spontaneously. The solubility of valeric acid in a mixture of equal volumes of glacial acetic acid and water may be employed to separate it from valeral and ethers, but not from amylic alcohol.\* The presence of butyric acid will be indicated by fractional distillation, and by the composition of the salt obtained by saturating the acid with carbonate of barium (see page 218); also by the reaction with cupric acetate (see next page).

REACTIONS OF VALERIC ACID AND VALERATES.—When valeric acid or a valerate is distilled with sulphuric acid and a little amylic alcohol, a fragrant ethereal liquid smelling of apples is obtained; this is the valerate of amyl. (See page 140.)

Metallic valerates are mostly soluble in water. The oxy-valerates of iron and bismuth are insoluble. Argentic and mercurous valerates are but slightly soluble, and valerate of aluminium is insoluble. Neither valeric nor butyric acid gives a precipitate with an aqueous solution of zinc acetate.

\* Valeric acid may be purified by dissolving in two equivalents of the crude acid one of neutral valerate of sodium, assisting the solution by a gentle heat. On standing in a cool place, crystals of an acid valerate of sodium are deposited, and on distilling this with sulphuric acid, and collecting the liquid which passes over between 125° and 138°, pure valeric acid is obtained.—*Lescœur*.



This fact distinguishes them from caproic acid, which throws down sparingly soluble zinc caproate as a white crystalline precipitate.

Valerate of barium is soluble in two parts of cold water, and is sparingly soluble in alcohol. Caprylate of barium requires 120 parts of cold water for solution, and is nearly insoluble in alcohol. Caprate of barium is almost insoluble in water.

When concentrated valeric acid is agitated with solution of cupric acetate, anhydrous cupric valerate separates in oily droplets, which, in from five to twenty minutes, crystallise as greenish-blue monoclinic prisms or octohedra of hydrated cupric valerate, moderately soluble in water and alcohol. The salt is less soluble in hot water than in cold, and hence the saturated solution becomes turbid when heated. This reaction distinguishes valeric from butyric acid, which forms with a not very dilute solution of cupric acetate an *immediate* precipitate or turbidity of cupric butyrate, of bluish-green colour, and finely crystalline in monoclinic prisms. In using this test for assaying valerates, the acid must first be obtained free by distilling the salt with a moderate excess of sulphuric acid.

Valerates are decomposed by acetic acid with formation of valeric acid and an acetate; they are also decomposed by tartaric, citric, or malic acid, but not by butyric acid. (The last statement probably applies to iso-valerates only.)

Valeric acid may be separated from most organic acids by converting it into the soluble valerate of lead. Acetic acid may be detected by neutralising any free acid with soda, and precipitating in the cold with excess of ferric chloride. In presence of acetic or formic acid, the filtered liquid will have a red colour. The insolubility of aluminium valerate might probably be employed for the separation of valeric from acetic or formic acid.

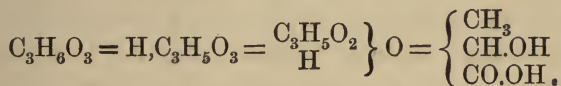
For other methods of approximately determining valeric acid and separating it from its homologues, see page 212, *et seq.*

VALERATES have been somewhat extensively used in medicine, especially the sodium, iron, zinc, and bismuth salts. They are all more or less liable to sophistication, which in some instances is of a very gross kind. Thus, samples of "valerate of zinc" are occasionally composed of the sulphate or acetate, and others have been met with which consisted of butyrate of zinc impregnated with oil of valerian. Similarly, tartrate or citrate of iron flavoured with valerian has been substituted for the valerate of iron, and the sulphate of quinine for the valerate. "Valerate of ammonium" has been prepared by saturating chloride of calcium with oil of valerian, and many similar frauds have been occasionally practised.

Most of the above adulterations may be readily detected. The substitution of butyrate of zinc for the valerate is best recognised by distilling the salt with sulphuric acid diluted with an equal measure of water, and then applying the cupric acetate and other tests to the distillate.

## LACTIC ACID.

*French*—Acide Lactique. *German*—Milchsäure.



Three modifications of lactic acid are known. Ordinary lactic acid, or ethylidene-lactic acid has the constitution shown above. It results from a peculiar fermentation of saccharine matter, and is produced in a great variety of reactions. It is present in sour milk, and is probably the principal free acid of sour beer. Para-lactic acid, sarco-lactic acid, or ethylene-lactic acid has the constitutional formula,  $\text{CH}_2\text{OH}-\text{CH}_2-\text{CO.OH}$ , and exists in the juice of lean meat.

Hydracrylic Acid, has probably the constitution  $\text{CH}_2\text{OH}-\text{CH}-\text{CHOH}$ .

$$\begin{array}{c} \text{CH}_2\text{OH}-\text{CH}-\text{CHOH} \\ \quad \diagdown \quad \diagup \\ \quad \quad \text{O} \end{array}$$

Hydracrylic acid is distinguished from the other varieties of lactic acid by the fact that, when heated, it yields no trace of lactide, but is resolved, almost without residue, into water and acrylic acid,  $C_3H_6O_3 = H_2O + C_3H_4O_2$ . Hydracrylic acid is more readily oxidised than the other varieties of lactic acid, giving off formic and much carbonic acid.

The differences between ordinary and paralactic acid are most observable in their calcium and zinc salts. (See pages 231, 232.) The free acids are hardly distinguishable. Ordinary lactic acid forms a deep-blue liquid with cupric sulphate, while paralactic acid is almost completely precipitated. They also differ in their products of oxidation, paralactic acid yielding malonic acid,  $C_3H_4O_4$ , while ordinary lactic acid is converted into aldehyde or acetic acid and carbonic or formic acid (see page 230). By hot nitric acid, lactic acid is converted into oxalic acid.

In its ordinary metallic salts, lactic acid is monobasic, but a second atom of hydrogen can be replaced by alcohol radicals.

Absolute lactic acid is a colourless, odourless, syrupy liquid, of a very acid taste. The specific gravity of the pure acid is 1.248; of that containing 75 per cent., 1.212. Lactic acid is not volatile without decomposition. At  $130^\circ C$ . it begins to decompose, and at about  $145^\circ C$ . dilactic acid,  $C_6H_{10}O_5$ , is formed, which, at a higher temperature, forms volatile lactide or lactic anhydride,  $C_3H_4O_2$ , and other products.

Dilactic acid and lactide are converted by prolonged boiling with water, and readily by solutions of caustic alkalis, into lactic acid. The lactide obtained by heating paralactic acid yields ordinary lactic acid when treated in this manner.

Lactic acid is miscible in all proportions with water, alcohol, and ether. It is but slightly soluble in chloroform. Glyceric acid,  $C_3H_6O_4$ , which resembles lactic acid, is insoluble in ether.

Lactic acid dissolves recently precipitated phosphate of calcium, and is frequently used for that purpose.

Concentrated sulphuric acid mixes with lactic acid without blackening it. On heating, a brown colour is developed, and much carbon monoxide evolved, a brown humus-like body being ultimately left.

Lactic acid does not reduce Fehling's solution, but rapidly decolorises permanganate, both in acid and in alkaline solutions. Lactate of silver is imperfectly reduced on boiling, with production of a blue-liquid and a brownish deposit.

Lactic acid may be separated from organic acids forming insoluble lead salts by precipitating the solution (previously neutralised if necessary) with acetate of lead, either with or without an addition of alcohol. Lead lactate remains in solution, and may be decomposed by sulphuretted hydrogen, when free lactic acid is obtained.

Many admixtures may be got rid of by saturating the free acid by barium carbonate. When the aqueous solution is evaporated and the residue treated with alcohol, many of the acids whose barium salts are soluble in water remain behind, whereas barium lactate dissolves in alcohol. Free lactic acid may be obtained by cautiously precipitating the solution of barium lactate with dilute sulphuric acid, and filtering.

When purified from all substances except those soluble in alcohol, the aqueous liquid containing free lactic acid may be saturated with oxide of zinc, evaporated to dryness, and the residue digested with alcohol. Lactate of zinc, insoluble in alcohol, remains, while the other matters dissolve. After drying at  $120^{\circ}\text{C}$ ., the residue may be weighed, when its weight, multiplied by  $\cdot 7402$ , gives that of the lactic acid. Paralactate of zinc dissolves readily in alcohol, so the above process is useless for the determination of paralactic acid. With ordinary lactic acid it yields fair approximate results, with careful manipulation and under favourable circumstances.

A method of determining lactic acid has been described by Messrs Chapman and Smith \* which is based on the fact that

\* *Journ. Chem. Soc.* xx. p. 173.



when heated with sulphuric acid and bichromate of potassium, it is decomposed thus—



Hence, one-third of the carbon of the lactic acid is evolved as carbon dioxide gas.\* The process is conducted as follows :— A flask, having a side tubulure, is connected by the latter with a small bulb-apparatus filled with concentrated sulphuric acid and immersed in cold water. The bulb-apparatus is connected with bulbs containing potash-solution (specific gravity 1·27), and beyond is a small tube containing fragments of caustic potash. The neck of the flask is closed by a perforated cork, through which is passed the stem of a stop-cock bulb-tube. A weighed quantity of the lactate or solution of lactic acid is placed in the flask, and 150 c.c. of a solution, containing 100 grammes of bichromate of potassium and 125 of concentrated sulphuric acid to the litre, are introduced through the bulb-tube. The contents of the flask are then heated by hot water (not by a flame). Carbonic acid gas is evolved, which bubbles through the sulphuric acid (and is thus freed from aldehyde vapour), and is absorbed by the potash solution. When no more bubbles pass, air is drawn through the apparatus, and the potash apparatus is removed and weighed. Its increase in weight, corresponding to the  $\text{CO}_2$  produced, multiplied by 2·045 gives the amount of lactic acid present. Alcohol (not in quantity), acetic acid, sulphuric acid, and many other substances have no disturbing influence on the results.

COMMERCIAL LACTIC ACID is liable to contain various impurities. Sulphuric acid and sulphates will be indicated on adding chloride of barium. Oxalic acid on adding lime water or acetate of calcium. Salts of calcium by oxalate of ammonium, and zinc by diluting the liquid and passing sulphuretted hydrogen, which will throw down white sulphide of zinc. Butyric acid, if present, will be re-

\* Paraclactic acid is acted on differently.

cognised by the smell of the sample, and by the fragrant pine-apple-like odour of ethyl butyrate evolved on heating the liquid with alcohol and strong sulphuric acid. Ethyl lactate boils at a high temperature and has very little odour.

**The Lactates** are all more or less soluble in water, but usually only sparingly so in the cold. All of them are insoluble in ether.

**CALCIUM LACTATE**,  $\text{Ca}''(\text{C}_3\text{H}_5\text{O}_3)_2$ , is obtained in crystals containing 5 Aq., when lactic acid is neutralised with lime or chalk and the liquid concentrated. It crystallises in small white mammillated tufts, which under the microscope appear as delicate needles, some of which look like bundles bound in the centre. From acid solutions, acid lactate of calcium crystallises in radiating trimetric needles. One part of calcium lactate dissolves in  $9\frac{1}{2}$  parts of cold water, and in all proportions in boiling water or alcohol. Calcium paralactate requires  $12\frac{1}{2}$  parts of cold water for solution, and contains 4 Aq.

**FEROUS LACTATE**,  $\text{Fe}''(\text{C}_3\text{H}_5\text{O}_3)_2$ , is a soluble salt crystallising in small needles with 3 Aq. The dry salt is permanent, but the solution rapidly oxidises. Ferrous lactate is not unfrequently adulterated, the substances used for the purpose being dried ferrous sulphate, milk-sugar, and starch. A sample of "lactate of iron," examined by M. Peltier, contained 25 per cent. of ferrous sulphate and 75 per cent. of milk-sugar. Ferrous sulphate can be readily detected by the copious precipitate produced on treating the solution of the sample with chloride of barium. Milk-sugar may be detected by rendering the solution alkaline by soda, passing sulphuretted hydrogen to precipitate the iron, filtering, adding Fehling's solution to the filtrate, filtering rapidly in the cold from the sulphide of copper, and heating the filtrate, when a yellow or red precipitate of cuprous oxide will be formed if milk-sugar be present. Starch may be detected in the portion of the sample insoluble in cold water, by the blue colour produced on addition of solution of iodine.

LEAD LACTATE,  $\text{Pb}''(\text{C}_3\text{H}_5\text{O}_3)_2$ , is freely soluble in water, sparingly soluble in cold but readily in hot alcohol, and slightly soluble in ether.

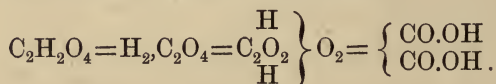
(Glycerate of lead is but slightly soluble in cold water.)

ZINC LACTATE,  $\text{Zn}''(\text{C}_3\text{H}_5\text{O}_3)_2$ , crystallises from concentrated solutions in shining crusts, from dilute solutions in four-sided prismatic needles. The crystals contain 3 Aq., which is lost rapidly at  $100^\circ\text{C}$ ., and above  $210^\circ\text{C}$ . the salt decomposes. Zinc paralactate crystallises with 2 Aq. in slender needles, which lose their water slowly at  $100^\circ\text{C}$ ., and give off empyreumatic vapours below  $150^\circ\text{C}$ . Paralactate of zinc is soluble in 6 parts of cold water and 2.2 of cold alcohol. The zinc salt of ordinary lactic acid requires 58 parts of cold or 6 of boiling water for its solution, and is insoluble in alcohol.

## OXALIC ACID.

*French*—Acide Oxalique; acide d'oseille.

*German*—Oxalsäure; Kleesäure.



Oxalic acid occurs ready formed in various plants—notably in the *oxalis acetosella* and in rhubarb. It is a frequent product of the decomposition of animal matters, occurring largely in diseased and occasionally in healthy urine, in certain urinary calculi, &c. It is a product of the action of nitric acid, alkaline permanganate, and other oxidising agents on various kinds of organic matter.

In commerce, oxalic acid is always produced by one of two reactions. The first is the oxidation of starch or sugar by moderately concentrated nitric acid, with subsequent separation and purification of the resultant oxalic acid by crystallisation, &c. This well-known and simple method is now almost replaced by the curious “sawdust process.” When starch,

sawdust, straw, bran, or other vegetable matter is heated with caustic potash, an oxalate is formed. Wheat-bran yields 150 per cent. of its weight of crystallised oxalic acid. Soda cannot be advantageously substituted for the potash, at least entirely, but with a mixture of the two alkalies very satisfactory results are obtained.

The product of the action is treated with water, and the solution treated with slaked lime. The alkalies are recovered in a caustic state, and the calcium oxalate is separated and decomposed with sulphuric acid, the resultant oxalic acid being separated by evaporation and crystallisation.

Oxalic acid usually occurs crystallised with two atoms of water,  $C_2H_2O_4 + 2H_2O$ , the crystals being monoclinic prisms. Exposed to dry air, or in vacuo over oil of vitriol, the crystals lose water, become opaque, and form a white powder. The acid may also be obtained anhydrous by exposure to a gentle heat ( $60^\circ$  to  $70^\circ$  C.) If at once heated to  $100^\circ$  C. the crystals melt, and the water is then much more difficult to drive off. The specific gravity of the crystals is 1.641 at  $3.9^\circ$  C.

Saturated solutions of oxalic acid lose acid at  $100^\circ$  C., and the anhydrous acid may be readily sublimed. This furnishes a convenient mode of obtaining the pure acid for analytical purposes. The acid should be previously rendered anhydrous by heating to  $60^\circ$  or  $70^\circ$  C., and the temperature of the retort must be kept as constantly as possible at  $157^\circ$  C. If allowed to rise to  $160^\circ$  C., much loss of acid occurs, and an inferior product is obtained, containing water and formic acid. The passage of a current of dry air greatly facilitates the sublimation.\*

\* Another simple method of purifying oxalic acid is to dissolve it in boiling hydrochloric acid containing 10 to 15 per cent. of real HCl. The liquid is stirred well, and then cooled quickly to get small crystals. These are washed with small quantities of cold water till but little hydrochloric acid remains in them. They are then redissolved in boiling water and recrystallised. The product so obtained is perfectly pure.



Oxalic acid is colourless and odourless, and completely volatile by heat without charring.

100 parts of water dissolve 8 parts of crystallised oxalic acid at 10° C. and 345 parts at 90° C.

The solution has an intensely sour taste, reddens litmus strongly, and in many respects acts like a mineral acid. It is very poisonous. It decomposes carbonates, phosphates, chromates, and various other salts, including fluorspar. (Powdered oxalic acid completely decomposes common salt or calcium chloride when the mixture is heated.)

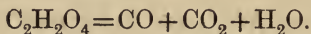
Prussian blue dissolves in aqueous oxalic acid to a clear blue liquid, often employed as a blue ink.

Solutions of oxalic acid are permanent in the dark, but when exposed to light the acid is rapidly decomposed.

Crystallised oxalic acid dissolves readily in cold and still more readily in boiling alcohol. It is but slightly soluble in ether, and is insoluble in chloroform, benzene, or petroleum spirit.

Oxalic acid bears the same relation to glycol,  $C_2H_4(OH)_2$ , that acetic acid does to ordinary alcohol.

Oxalic acid is not affected by boiling with moderately strong nitric or hydrochloric acid. When heated with concentrated sulphuric acid, phosphoric acid, or either of the chlorides of phosphorus, it splits up thus:



Cold sulphuric acid has no action on oxalic acid. When heated with glycerin, oxalic acid yields carbonic acid at a moderate heat, and formic acid at a higher temperature. This is the method commonly employed for producing formic acid.

Chlorine combines with dry oxalic acid to form a compound of the formula  $C_2H_2O_4Cl_2$ , which is split up by water into hydrochloric and carbonic acids.

Dioxides of manganese and lead oxidise oxalic acid to carbonic acid. Auric chloride and acid solutions of permanganates react similarly. In presence of a large excess

of alkali, oxalic acid is not oxidised by permanganate.—(*Wanklyn.*)

REACTIONS OF OXALIC ACID AND OXALATES.—An aqueous solution of oxalic acid presents the following characters:—

1. On addition of lime water or solution of calcium acetate, a white precipitate of calcium oxalate,  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ , is formed. The precipitate is very insoluble in water, and not sensibly soluble in acetic or other organic acids. It is readily soluble in dilute mineral acids. It is decomposed by boiling with excess of carbonate of sodium solution, with formation of insoluble calcium carbonate and soluble sodium oxalate. On gentle ignition, calcium oxalate evolves carbon monoxide,  $\text{CO}$ , and leaves calcium carbonate. No blackening occurs in this reaction. Solutions of soluble oxalates give the same reaction as oxalic acid with lime water or calcium acetate, and react with calcium sulphate or chloride in addition. If previously neutralised by ammonia, oxalic acid solutions are precipitated by the two latter reagents.

2. With solutions of barium, oxalic acid and oxalates react in a similar manner as with solutions of calcium, but the resultant barium oxalate is not so insoluble in water or acetic acid as the calcium salt.

3. On addition of dilute sulphuric acid and manganese dioxide, warm solutions of oxalic acid and oxalates produce effervescence, owing to the formation of carbon dioxide gas, according to the reaction  $\text{H}_2\text{C}_2\text{O}_4 + \text{O} = \text{H}_2\text{O} + 2\text{CO}_2$ . The gas may be proved to be carbon dioxide by its reaction with lime water.

4. In presence of dilute sulphuric acid, warm solution of oxalic acid rapidly decolorises potassium permanganate. From strong solutions, the resultant carbon dioxide escapes with effervescence.

DETERMINATION OF OXALIC ACID.—Oxalic acid may be determined with considerable accuracy by either of the following methods, the details of which may be found in most works on quantitative analysis:—

1. By precipitation as calcium oxalate. The solution should be hot and dilute. In the absence of other acids forming insoluble or nearly insoluble calcium salts (*e.g.*, sulphates, tartrates, citrates, phosphates), the solution may be exactly neutralised by ammonia, and calcium chloride added. Any phosphate may be separated by digesting the precipitate with cold dilute acetic acid. In presence of sulphates, calcium sulphate should be employed as a precipitant. It is frequently preferable to have the solution acid with acetic acid, or to precipitate the acid solution with calcium acetate, so as to avoid the coprecipitation of other calcium salts. Almost all calcium salts are soluble in acetic acid, except the oxalate, racemate, and fluoride. Racemates may be previously removed by precipitation with potassium acetate in presence of alcohol. The separation of oxalates and fluorides does not occur in practice, but if required, the oxalate can be determined by titrating the precipitate with standard permanganate. The precipitate of calcium oxalate, however produced, is to be well washed and then treated in one of the following ways:—

- a.* It is dried at  $100^{\circ}\text{C.}$ , and weighed as  $\text{CaC}_2\text{O}_4$ .
- b.* It is ignited, moistened with carbonate of ammonium, again gently ignited, and weighed as  $\text{CaCO}_3$ .
- c.* It is moistened on the filter with strong sulphuric acid, and the whole ignited and weighed as  $\text{CaSO}_4$ .
- d.* It is ignited thoroughly, and the resultant carbonate titrated with standard acid.
- e.* The filter is placed in a beaker together with water and dilute sulphuric acid, and the liquid is titrated with standard permanganate.

Of these methods, the two last are perhaps the best, because they are the least affected by any impurity in the precipitate. Process *e.* aims at the direct estimation of the oxalate, and may be applied to a precipitate containing phosphate, carbonate, or sulphate; tartrate, racemate, and most organic salts must be absent from the precipitate.

2. By treatment with dilute sulphuric acid and manganese dioxide in a carbonic acid apparatus. This process is conducted precisely as in the valuation of a manganese ore, except that excess of manganese dioxide is used instead of excess of the oxalate. 44 parts by weight of  $\text{CO}_2$  lost by the apparatus represent 63 of crystallised, or 45 of anhydrous oxalic acid.

3. By titration with standard permanganate. The solution of the oxalate must be free from other readily oxidisable bodies, and should be warm, dilute, and pretty strongly acidulated with sulphuric acid. The permanganate is added gradually, with constant stirring, until the liquid acquires a permanent pink tint. The permanganate is preferably standardised with pure oxalic acid. Decinormal permanganate, containing 3.162 grammes  $\text{KMnO}_4$  to the litre, is a suitable strength. Each c.c. of this solution will oxidise .0063 grammes of crystallised, or .0045 grammes of anhydrous oxalic acid. The process can be employed for titrating a precipitate of calcium oxalate.

**Toxicological Examination for Oxalic Acid.**—Oxalic acid and its solutions are violently *poisonous*. The same is true of the soluble oxalates. If a very concentrated solution of free oxalic acid be taken internally, an immediate burning pain in the stomach is observed, together with cramps and drawing up of the legs, and vomiting of dark and perhaps bloody coffee-coloured matters. The patient often complains that the throat feels as if tightly bound with a cord. Bloody purging next occurs, the tongue becomes sore, and the mouth swollen and usually white. Numbness and tingling of the legs, twitchings of the face, convulsions and delirium will be more or less marked, while the circulation becomes very depressed, and respiration slow and spasmodic.

With weaker solutions, the above effects are less marked; death may be almost instantaneous, or may be postponed for a considerable time. Half an ounce is an ordinary poisonous dose, but a much smaller quantity has proved fatal.



The proper antidote for oxalic acid is whiting, chalk, or magnesia, suspended in a small quantity of milk.

After death, the mouth, throat, and gullet will usually be found shrivelled and easy of removal. The stomach, which is frequently contracted, often contains an intensely acid, brown, gelatinous liquid. The mucous membrane, if death be rapid, may appear soft and pale, but if death be long delayed it is usually partly blackened, other portions being intensely congested, the surface peeling off and the coats underneath being gangrenous. Throughout the whole body, except the stomach and gullet, the blood is fluid. Occasional cases are on record in which morbid appearances have been nearly or entirely absent.

In cases of poisoning by oxalic acid, supposing no antidote to have been administered, the contents of the stomach will usually be intensely acid. (Of course, moderate acidity is the *normal* condition.)

The urine should always be examined when poisoning by oxalic acid is suspected. It should be allowed to stand in a conical glass. The clear solution is subsequently decanted, and the sediment examined under the microscope for octohedral crystals of calcium oxalate. These should be found in abundance, and may also be identified by chemical tests.

THE TOXICOLOGICAL DETECTION OF OXALIC ACID may be effected in the following manner:—The contents of the stomach, if acid, are digested with warm water and strained through muslin, or, if possible, through paper. To the clarified liquid, *excess* of solution of basic lead acetate is added, which will throw down any oxalic acid, together with colouring and other organic matter. The precipitate is washed, well suspended in water, and decomposed by a current of sulphuretted hydrogen. The liquid is again filtered, when the filtrate will probably be sufficiently pure to admit of the application of the characteristic tests for oxalic acid. Of these, the most satisfactory for toxicological purposes are the production of crystals of the free acid, and the formation of a precipitate having the properties of

calcium oxalate on addition of calcium chloride and ammonia, or of calcium acetate alone.

Soluble neutral oxalates can readily be detected by the above process, but a modified method must be used if a compound of calcium or magnesium has been administered as an antidote. In such a case, the contents of the stomach should be boiled for an hour or two, without previous filtration, with a strong solution of alkaline carbonate. The liquid is filtered from the residual carbonate of earthy-metal, acidulated with acetic acid, and then precipitated with acetate of lead as above described.

**Commercial Oxalic Acid** is now so cheap that it is rarely, if ever, purposely adulterated; nevertheless, various impurities are frequently present, owing to careless manufacture or imperfect purification.

ORGANIC MATTERS other than oxalic acid are recognised by the charring or darkening of the sample when heated.

FIXED MINERAL IMPURITIES are left as a residue on igniting the sample in the air. If the ignited residue effervesce on addition of dilute acid, an acid oxalate is present in the sample. Very sensible quantities of lead and other heavy metals are sometimes met with.\*

SULPHURIC ACID AND ACID SULPHATES are sometimes present in oxalic acid in considerable quantity. The solution of such samples gives a white precipitate of  $\text{BaSO}_4$  on addition of barium chloride. The same impurities are very common in commercial ammonium oxalate.

**Oxalates.**—These salts require but little special description. The alkali-metals form three classes of oxalates, the potassium salts having the formulæ  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ;  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ; and  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ . The acid salts are the least soluble. The oxalates of most other metals are insoluble, or nearly insoluble, in water. This is true of the oxalates of barium, strontium, calcium, copper, magnesium, manganese, cobalt, nickel, zinc,

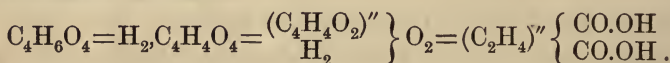
\* In a sample of oxalic acid sold as specially purified for analytical purposes, I found as much as 6.3 per cent. of oxide of lead.

lead, silver, &c. The first four of these retain 1 atom of water on drying at  $100^{\circ}$  C. The remainder retain 2 atoms, with the exception of the lead and silver salts, which are anhydrous. Ferrous oxalate is but sparingly soluble, but ferric oxalate is readily so, at least in presence of free oxalic acid; hence the use of oxalic acid for removing ink-stains and dissolving Prussian blue. All the insoluble oxalates are soluble in dilute nitric acid, but they are generally insoluble in acetic acid. The determination of the oxalic acid may be readily effected by the methods described on pages 236 and 237.

On ignition, oxalates of the metals of the alkalies and alkaline-earths evolve carbon monoxide gas, and leave the corresponding carbonates. These may sometimes be further decomposed if the temperature be excessive ( $\text{CaC}_2\text{O}_4 = \text{CaO} + \text{CO} + \text{CO}_2$ ). Oxalates of the heavy metals, when heated to redness in a close vessel, usually leave the free metal and evolve carbon dioxide gas ( $\text{NiC}_2\text{O}_4 = \text{Ni} + 2\text{CO}_2$ ). This reaction occurs even at  $100^{\circ}$  C. in the case of gold; hence, gold is reduced from its solutions by boiling with an oxalate.

Pure oxalates do not char on ignition.

### SUCCINIC ACID.



—Succinic acid occurs ready formed in amber and in certain lignites, is produced during the alcoholic fermentation of sugar, and by the fermentation of malic acid and many other substances, especially under the influence of putrefying casein. Succinic acid is also produced by the action of nitric acid on the fatty acids and their glycerides, and it exists ready formed in several plants.

Succinic acid bears the same relation to butylenic alcohol that oxalic acid does to ethylenic alcohol (glycol), and may be produced from butylenic alcohol by oxidation. It may also be obtained by the deoxidation of tartaric or malic acid, which



contain respectively two and one atom more of oxygen than does succinic acid.

Succinic acid may be obtained by the dry distillation of amber, the watery distillate being filtered while hot to separate oil, when crystals of succinic acid are deposited on cooling, and may be purified by boiling with nitric acid, followed by recrystallisation from water.

Succinic acid crystallises in colourless, oblique rhombic prisms or plates. When heated to  $130^{\circ}$  C. it emits suffocating fumes and at  $180^{\circ}$  melts. When the heat is increased to  $235^{\circ}$  C. the acid boils and sublimes as succinic anhydride,  $C_4H_4O_3$ , which melts at  $120^{\circ}$  C. When heated strongly in the air, succinic acid burns with a blue smokeless flame.

Succinic acid is soluble in about 13 parts of cold and  $2\frac{1}{2}$  of boiling water. It dissolves in alcohol and in ether, but is insoluble in chloroform or benzene. Nitric acid, chlorine, and chromic acid have no action on succinic acid. Permanganate has no action on a cold acid solution, but hot permanganate in presence of free alkali produces oxalic acid.

In its analytical reactions, succinic acid somewhat resembles benzoic acid, but differs from it in not being precipitated from a strong solution of its salts by hydrochloric acid; in being precipitated by ammoniacal chloride of barium even from a dilute solution; and by being insoluble in chloroform, and therefore not removable from an acid solution by agitation with that liquid. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

Ferric chloride, if first treated with as much dilute ammonia as it will bear without precipitation, precipitates from neutral solutions of soluble succinates bulky brownish-red basic ferric succinate. Benzoates, under similar circumstances, give a flesh-coloured precipitate, and cinnamates a yellow. The precipitate may be filtered off, washed, and boiled with excess of dilute ammonia. The filtered liquid, if mixed with barium chloride and an equal bulk of alcohol, gives a white precipitate



of barium succinate. By the above combination of reactions, succinic acid may be readily identified and separated from other organic acids.\* The process might possibly be made quantitative. For such a purpose, sodium acetate should be added to the liquid containing the iron precipitate, and the whole boiled, the precipitate produced being first boiled and then washed with dilute ammonia, the ammoniacal liquid being then precipitated by alcohol and chloride of barium.

For the determination of the succinic acid in wine M. Maumené recommends the following process:—To 1 litre of the sample add sufficient albumin or raw hide to precipitate all the tannin. The filtered liquid is concentrated and treated with hydrated oxide of lead till the colour is entirely removed. The precipitate is boiled for a long time with a 10 per cent. solution of ammonium nitrate, and the liquid filtered. The filtrate is treated with sulphuretted hydrogen, the precipitate filtered off, the filtrate concentrated to 100 c.c., and exactly neutralised with ammonia. Perfectly neutral ferric chloride is then added, the precipitate well washed, ignited, and the residual  $\text{Fe}_2\text{O}_3$  calculated to succinic acid by multiplying the weight found by the factor 1.978.

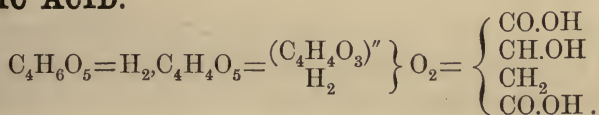
COMMERCIAL SUCCINIC ACID has usually more or less a brown or yellow colour, and smells somewhat of the empyreumatic oil of amber. It is not unfrequently adulterated with sal-ammoniac, cream of tartar, oxalic acid, boric acid, barium sulphate, &c. The incomplete volatility of the sample will suffice to indicate the presence of some of these, and the nature of the residue left on ignition will show the kind of adulterant used. Cream of tartar leaves potassium carbonate on ignition; it has been found in succinic acid to the extent of 50 per cent. of the sample. Oxalic Acid and Sal-ammoniac are volatile on

\* For methods of separating succinic acid from malic acid, see the latter (pages 244 and 245).

ignition, but they may readily be recognised in the wet way, by the formation of the insoluble oxalate of calcium and chloride of silver. If a chloride be found in quantity by adding nitrate of silver in presence of nitric acid, the presence of ammonium must be proved before assuming the presence of sal-ammoniac.

FICTITIOUS SUCCINIC ACID has been prepared by adding a little oil of amber to tartaric acid, sal-ammoniac, or acid sulphate of potassium.

### MALIC ACID.



This acid is contained in apples, pears, and most fruits used for domestic purposes. It is usually prepared from rhubarb stalks or mountain-ash berries.

Malic acid crystallises in groups of four- or six-sided prisms, which are colourless and odourless, and readily fusible. Malic acid is deliquescent and readily soluble in water, alcohol, and ether. The aqueous solution has an agreeable acid taste, and becomes mouldy on keeping. In contact with ferments, especially putrid cheese, the solution of malic acid yields succinic acid,  $\text{C}_4\text{H}_6\text{O}_4$ , and acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ . Sometimes butyric acid is produced.

When heated in a small retort to about  $180^\circ \text{C}$ ., free malic acid melts and evolves vapours of maleic and fumaric acids, which crystallise on the cooler parts of the retort and receiver. Fumaric acid,  $\text{C}_4\text{H}_4\text{O}_4$ , forms slowly at  $150^\circ \text{C}$ ., and mostly crystallises in the retort, in broad, colourless, rhombic or hexagonal prisms, which vaporise without melting at about  $200^\circ \text{C}$ ., and are soluble in 250 parts of cold water, and easily in alcohol and ether. Maleic acid,  $\text{C}_4\text{H}_4\text{O}_4$ , is the chief product if the temperature be suddenly raised to  $200^\circ \text{C}$ . This body crystallises in oblique rhomboidal prisms, which melt at

130°, vaporise at about 160° C., and are readily soluble in water and alcohol. The behaviour of malic acid on heating is of value owing to the few characteristic tests for this acid.

Native malic acid exerts a negative rotatory action on a ray of polarised light.\* By the action of hydriodic acid (in a sealed tube), malic acid is converted into succinic acid. Nitric acid and alkaline solution of permanganate oxidise malic acid. Concentrated sulphuric acid darkens malic acid and malates very slowly on warming. When boiled with dilute sulphuric acid and bichromate of potassium, malic acid evolves an odour of ripe fruit.

None of the malates are quite insoluble in water, but few are soluble in alcohol. Solution of calcium chloride does not precipitate malic acid or malates in the cold (distinction from oxalic and tartaric acids); only in neutral and very concentrated solutions is a precipitate formed on boiling (citrates are precipitated from neutral boiling solutions by calcium chloride, unless the liquid is very dilute). The addition of alcohol after chloride of calcium produces a bulky, white precipitate of calcium malate,  $\text{CaC}_4\text{H}_4\text{O}_5$ , even in dilute neutral solutions. Thus, if the liquid be filtered first cold (to remove oxalic and tartaric acids), and then boiling hot (to remove citric acid), the malic acid can be precipitated on addition of two volumes of alcohol. This precipitate may contain calcium sulphate or succinate, but will be free from formate,† acetate, benzoate, &c. On boiling the precipitate with a moderate quantity of water, the malate will be dissolved, and tannate and sulphate left almost wholly behind. The precipitate produced by calcium chloride and alcohol may also be tested for malic acid (after drying it to get rid of all trace of alcohol) by decomposing it with dilute sulphuric acid, and boiling the filtered liquid with a *small* quantity of potassium anhydrochromate (bichromate). If the liquid re-

\* Artificial malic acid is inactive.

† If more than two volumes of alcohol be added, calcium formate may be precipitated.

main yellow, succinic acid alone is likely to be present ; but if a green colour is produced without any odour being developed, citric acid is probably present either with or without succinic acid. If the liquid acquires a green colour, and evolves an odour of ripe fruit, malic acid is present, and possibly either or both succinic and citric acids in addition.

Solution of acetate of lead precipitates malic acid, more perfectly after neutralisation with ammonia, as a white (and frequently crystalline) precipitate of lead malate,  $\text{PbC}_4\text{H}_4\text{O}_5$ , which, on boiling a few minutes, melts under the liquid to a transparent, waxy semi-solid. This characteristic reaction is obscured by the presence of other organic acids. The precipitate is very sparingly soluble in cold water, somewhat soluble in hot water. Malate of lead is soluble in strong ammonia, but is not readily dissolved by a slight excess. (Distinction from tartrate and citrate.) Malate of lead dissolves in ammonium acetate, and on mixing the liquid with two volumes of alcohol is reprecipitated. (Any succinate of lead remains in solution.) The precipitate may be washed with a mixture of 2 measures of alcohol and 1 of water.

If the precipitate of malate of lead be treated with excess of ammonia, dried on the water-bath, moistened and triturated with alcoholic ammonia, and then treated with absolute alcohol, only malate of ammonium dissolves ; ammonium citrate, tartrate, oxalate, &c., being insoluble in absolute alcohol. Malic acid may be separated from other organic acids in solution by adding ammonia in slight excess, and then 8 or 9 volumes of strong alcohol, which precipitates all but the malate of ammonium. The method may be conveniently applied to the solution of the free acids obtained by suspending the lead salts in water and passing sulphuretted hydrogen through the liquid.

If the alcoholic solution of ammonium malate be precipitated by lead acetate, and the malate of lead obtained filtered



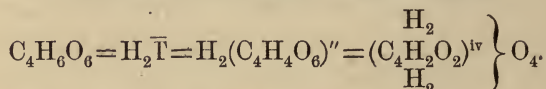
off, and washed with alcohol, dried at 100, and weighed, the weight obtained, multiplied by 0.3953, gives the quantity of malic acid present.

For the determination of malic acid in wine, 100 c.c. should be precipitated with a slight excess of lime water; the filtrate is concentrated to one-half its bulk, and absolute alcohol added in excess; the precipitate, consisting of calcium malate and sulphate, is collected on a filter, washed with proof-spirit, dried, and weighed. If the calcium sulphate be next determined by dissolving the precipitate in water, precipitating the solution by barium chloride, and multiplying the weight of barium sulphate obtained by .5837, the difference may be regarded as calcium malate, 172 parts of which correspond to 134 of malic acid.

## TARTARIC ACID.

*French*—Acide Tartarique.

*German*—Tartarsäure, Weinsteinssäure.



Tartaric acid occurs, either free or combined, in various plants. The grape is the only source from which it is commercially obtained. The deposit formed on the sides and bottom of the vessels in which wine is manufactured consists largely of calcium and potassium tartrates. After purification, it is treated with chalk and calcium sulphate, by which a nearly insoluble calcium tartrate is produced, and this, when decomposed with sulphuric acid, yields free tartaric acid, which is obtained in crystals by cooling the concentrated liquid.

Five distinct modifications of tartaric acid exist. Their chief physical and chemical differences are as follow:—

*a.* DEXTRO-TARTARIC, or ORDINARY TARTARIC ACID, forms anhydrous, hemihedral, rhombic crystals, the aqueous solution

of which turns the plane of polarisation of a luminous ray to the *right*. The crystals fuse at 135° C., have a density of 1.74 to 1.75, and are readily soluble in absolute and in aqueous alcohol.

In the following article, ordinary tartaric acid and its salts are always referred to unless some special prefix is employed.

*b.* **LEVO-TARTARIC, or ANTI-TARTARIC ACID**, forms anhydrous, hemihedral, rhombic crystals, the aqueous solution of which turns the plane of polarisation of a luminous ray to the *left*.

*c.* **RACEMIC, or PARA-TARTARIC ACID**, forms hydrated, holohedral, triclinic crystals of  $\text{H}_2\bar{\text{T}}, \text{H}_2\text{O}$ , which are optically *inactive*. The crystals have a density of 1.69, and are soluble in five parts of cold water, and with difficulty in cold alcohol. The calcium racemate is less soluble in water than calcium dextro-tartrate, and is also distinguished by its insolubility in acetic acid, and in chloride of ammonium solution.\*

*d.* **INACTIVE, or MESO-TARTARIC ACID**: optically inactive, but not resolvable in *a.* and *b.* acids.

*e.* **META-TARTARIC ACID**: produced by fusing the ordinary variety. It is deliquescent and uncrystallisable. Its solution and those of its salts are converted by boiling into those of the ordinary modification.

When heated to 205° C., tartaric acid loses the elements of water, and is converted successively into substances of the formula  $\text{C}_8\text{H}_{10}\text{O}_{11}$ ;  $\text{C}_4\text{H}_4\text{O}_5$ ; and  $\text{C}_5\text{H}_8\text{O}_4$ ; it ultimately carbonises and emits a smell resembling that of burnt bread or sugar.

Tartaric acid is very soluble in water and alcohol, but

\* Racemic acid can be prepared by mixing *a.* and *b.* tartaric acids, and can be resolved into them by appropriate methods. According to Staedel, crystals of natural acemic acid differ from the artificial product by not disintegrating on exposure to air. Anhydrous artificial racemic acid is stated to fuse at 198°, and the natural at 201° C.

insoluble in ether. The aqueous solutions have the following densities as determined by H. Schiff:—

Percentage by weight of tartaric acid.	Density at 15° C. (= 59° F.)
33	1.1654
22	1.1062
14.67	1.0690
11	1.0511
7.33	1.0337
3.67	1.0167

Aqueous solutions of the acid (especially when dilute) gradually decompose with growth of fungus. Cream of tartar and other tartrates decompose when kept in a moist state.

Tartaric acid contains two atoms of hydrogen replaceable by metals,\* and hence forms two classes of salts. Few of the metallic tartrates are readily soluble in water, and all are insoluble in alcohol. The greater number of tartrates, except tartrate of mercury, are soluble in ammonia.

#### DETECTION AND DETERMINATION OF TARTARIC ACID.

1. Tartaric acid and tartrates are charred when heated with concentrated sulphuric acid.

2. Soluble tartrates in neutral solution give white calcium tartrate on addition of chloride of calcium. The precipitate is nearly insoluble in cold water; soluble in many ammoniacal salts; soluble (after washing) in cold solution of sodium hydrate, but reprecipitated on boiling; soluble in acids (including acetic); and converted by heating with a neutral solution of cupric chloride into insoluble cupric tartrate. (Citrate of calcium yields soluble cupric citrate).

3. The reducing action of tartaric acid on solutions of silver is an extremely delicate test when properly applied, but is remarkably liable to failure if the proper conditions are not carefully observed. The solution of tartaric acid, or the tartrate of alkali-metal (all other metals being first removed),

\* Two additional atoms are replaceable by alcoholic or acid radicals.

is rendered acid with nitric acid, *excess* of silver nitrate added, and any precipitate filtered off. To the solution *very dilute* ammonia is added until the precipitate at first formed is nearly redissolved. The solution is again filtered, and the filtrate heated nearly to boiling for a few minutes, when a brilliant metallic mirror will be deposited on the sides of the tube. Citric acid does not reduce silver under similar circumstances, except on continued boiling.

4. Tartaric acid prevents the precipitation of many metallic solutions by alkalies, stable double tartrates being formed. For the separation of heavy metals from tartrates, sulphuretted hydrogen or sulphide of sodium must be employed, according to the metals present. The filtrate may be concentrated, and any barium, strontium, calcium, or magnesium present thrown down by boiling with carbonate of sodium. Aluminium is not separated by either of the above precipitants, but the tartaric acid can be detected and estimated in the solution without removing it.

5. The best method of determining tartaric acid by direct estimation is to precipitate it in the form of potassium-hydrogen tartrate ( $\text{KHT}$ ). (For the properties of this salt, see page 258.) When the free acid is to be determined, either alone or mixed only with citric acid, no better process can be employed than that described on page 264. For the determination of tartaric acid in tartrates, and in the various natural and artificial products of tartaric acid manufactories, the processes of Mr Warington, described on page 250, *et seq.*, are by far the best.

6. Like the corresponding salts of other organic acids, the tartrates of the light metals leave on ignition a residue of carbonate or oxide of the contained metal, and by dissolving this residue in standard acid and ascertaining the amount of acid neutralised by titrating the excess with standard alkali, an accurate estimation of the metal can be obtained, and if it be known whether the tartrate was originally an acid or a



neutral salt, a determination of the tartaric acid itself is obtained.

7. Tartaric acid and acid tartrates neutralise alkalies completely, and litmus affords a perfectly sharp indication of the end of the reaction. Hence the ordinary processes of alkalimetry are applicable to tartaric acid and tartrates.

The tartaric acid in tartrates of organic bases may generally be determined by precipitation as acid tartrate of potassium.

The tartrates of the alcohol radicals are unimportant. Tartrate of ethyl may be decomposed by heating with alcoholic potash, and the acid tartrate of potassium subsequently precipitated by adding excess of acetic acid. (See also page 142.)

COMMERCIAL TARTARIC ACID is liable to contain the same impurities as citric acid, and is examined in a similar manner. (See page 263, *et seq.*)

**Tartaric Acid Liquors** are the liquids resulting from the decomposition of calcium tartrate by sulphuric acid. They are of a very complex character, containing free tartaric acid, sulphuric acid and sulphates of calcium, potassium, iron, and aluminium, phosphates, and various organic acids and bodies of an indefinite nature. Their analytical examination is limited to the determination of the tartaric and free sulphuric acid, and, in some cases, of the total organic acids.

The determination of the tartaric acid is best effected by precipitation as the acid potassium salt. Acetate of potassium is the best reagent for pure liquors, but is inapplicable in presence of iron or aluminium. Citrate of potassium is without this objection, and is employed by Warrington in the following manner:—

A quantity of liquor, containing from 2 to 4 grammes of tartaric acid, and of 30 to 40 c.c. in volume, is treated with a saturated aqueous solution of tripotassic citrate,\* added drop by drop with constant stirring. As soon as the free sulphuric

\* Obtained by neutralising citric acid by pure potash or potassium carbonate.

acid is satisfied, the precipitate begins to appear in streaks on the sides of the glass. In presence of much sulphuric acid, a fine precipitate of potassium sulphate will precede the formation of the acid tartrate, but is readily distinguished from it. When the streaks begin to appear, 1 c.c. of citrate solution is added for every gramme of tartaric acid supposed to be present. A great excess should be avoided. Should a gelatinous precipitate be formed, the experiment is repeated with a previous addition of some citric acid. After standing twelve hours, the precipitate is collected on a small filter, washed two or three times with a 5 per cent. solution of potassium chloride, then with single washings of 50 per cent. and 70 per cent. alcohol, and finally with 80 to 90 per cent. alcohol till the washings are no longer acid to tincture of litmus. The filter and precipitate are finally transferred to a beaker, and the amount of tartaric acid present is determined by titration with standard alkali. Instead of washing the precipitate in the above manner, a saturated aqueous solution of acid potassium tartrate, containing 5 per cent. of potassium chloride, may be employed, the washing being continued till the acidity of the filtrate is no greater than that of the wash-water. A correction should in this case be applied for the acidity of the wash-water retained by the filter.\* The presence of potassium sulphate in the precipitate is of no consequence, as it has no neutralising power. Alum interferes, and, therefore, in presence of aluminium, the second method of washing is to be preferred. Mr Warrington's test experiments gave very satisfactory results.

Racemic Acid, if present, will be estimated as tartaric acid by the above method. Inactive and meta-tartaric acid are only imperfectly precipitated, owing to the greater solubility of their potassium salts. Oxalic acid does not interfere with the results.

The determination of the free sulphuric acid in tartaric acid

\* See note on page 256.

liquors is troublesome, owing to the insolubility of potassium and calcium tartrates in alcohol, and to the occasional presence of alum. Thus, if mixed solutions of potash-alum and tartaric acid are treated with alcohol, potassium hydrogen tartrate and alum are precipitated, and the liquid contains free sulphuric acid, which was not present originally. A similar reaction occurs if sulphate of calcium be substituted for the alum. These errors are removed when the quantity of free sulphuric acid in the liquor is sufficiently great, and will occur in practice merely in the case of new liquors of bad quality. The following process is recommended by Warington for the determination of the free sulphuric acid. From 5 to 20 c.c. of the liquor is slowly dropped into 100 c.c. of 90 per cent. alcohol, with continual stirring. (If the liquor be concentrated and of bad quality, it should be previously diluted with an equal bulk of water.) The precipitate contains sulphates, aluminium phosphate, &c. The solution is filtered after 24 hours, the precipitate washed with alcohol, and the filtrate precipitated with an alcoholic solution of calcium chloride. The  $\text{CaSO}_4$  is separated by filtration or decantation, and, without washing, dissolved in hydrochloric acid. On addition of barium chloride to the highly diluted and hot solution, barium sulphate is precipitated. 233 parts of  $\text{BaSO}_4$  correspond to 98 parts of free  $\text{H}_2\text{SO}_4$ .

For the determination of the total organic acids in tartaric acid liquors, Mr Warington gives the following method. For an explanation of the steps of the process, the original paper must be consulted.\*

Exactly neutralise a known measure of the liquor with standard alkali, evaporate to dryness, and ignite at a low temperature till the carbon is nearly consumed. Treat the ash with a known quantity of standard sulphuric acid, heat and decant, and treat the insoluble residue with more standard acid, concentrating, if necessary, to effect solution of the phos-

\* *Journ. Chem. Soc.* 1875, page 982, *et seq.*



phates. Treat the mixed cold concentrated solutions with sufficient Rochelle salt ( $\text{KNaT}$ ) to keep any alumina in permanent solution, and then titrate the solution with standard alkali. The amount of standard sulphuric acid neutralised by the ash is the exact equivalent of the total organic acid in the liquor taken, and each c.c. of normal acid neutralised represents .075 grammes of organic acid expressed in terms of tartaric acid. Oxalic acid has been detected in old tartaric liquors, and the presence of meta- and di-tartaric acids is probable, but the subject requires further investigation. The presence of meta-tartaric and racemic acids seems in some way dependent on the alumina.

**Lees; Argol; Tartar.**—These are the materials from which tartaric acid and tartrates are extracted. The lees is the solid matter collected from the bottom of the vessels in which the grape-juice is fermented in the manufacture of wine. Argol is the thin crystalline crust deposited on the sides of these vessels. Tartar is extracted from the two former by treatment with hot water, and crystallisation from the liquid. The sparingly soluble  $\text{KHT}$  and  $\text{Ca}''\text{T}$  are deposited. These salts are still less soluble in alcohol than in water; hence the formation of tartarous deposits containing them during the fermentation of the grape-juice.

The composition of lees is greatly altered by "plastering" the wine. This process consists in adding to the wine some "Yeso," which is essentially a sulphate of calcium containing some carbonate. "Spanish earth," a kind of readily decomposed clay, is sometimes employed. The result is, that in plastered lees the tartrate is chiefly the neutral calcium, instead of the acid potassium salt. The total tartaric acid in lees is usually from 24 to 32 per cent. Lees contain from 30 to 40 per cent. of indefinite vegetable matter, the remainder being tartrates, sulphates (in plastered lees), sometimes lumps of plaster, water, &c. Argol exhibits some variety of composition, the tartaric acid ranging from 40 to 70 per cent., and being



always present chiefly as acid potassium tartrate. Very low argols resemble superior lees, while first-class argols are equal to ordinary tartar. In argol, globules of sulphur are sometimes found; they are due to the sulphur burnt in the casks before introducing the wine.

Tartar consists essentially of acid tartrate of potassium with from  $1\frac{1}{2}$  to 6 per cent. of neutral tartrate of calcium. Small quantities of sand, alumina, magnesia, and water are frequently present.

Tartar is sometimes adulterated to a considerable extent. The sulphates and chlorides of potassium and calcium are occasionally used. Alum is also employed for the purpose, and native sulphate of barium has been met with. The latter is detected by examining the residue left on dissolving the sample in hydrochloric acid; both the microscopical and chemical characters may be employed. It may also be detected by igniting the sample, treating the ash with water, dissolving any residual  $\text{BaCO}_3$  and  $\text{CaCO}_3$  in dilute acid, and adding calcium sulphate to the solution. Alum is recognised by the presence of more than traces of sulphates, and by the presence of alumina in the ash. No precipitate can be obtained by ammonia in presence of the tartrate; but alumina may be detected by neutralising the hot solution of the sample with soda, and boiling with a little acetic acid and excess of sodium phosphate. Any aluminium is thrown down as phosphate, tartrates having scarcely any solvent action on the precipitate at a boiling heat, and in presence of excess of phosphoric acid. Alum may be dissolved out of tartar by treating the finely-powered sample with a cold, saturated, aqueous solution of potassium-hydrogen tartrate, containing 5 per cent. of potassium chloride.

Various methods have been proposed and employed for the assay of lees, argols, &c.; the following are the best:—

a. The tartaric acid existing as  $\text{KHT}$  is determined by titrating a hot aqueous solution of 5 grammes of the sample

with standard alkali. Each c.c. of normal alkali corresponds to .150 grammes of  $\text{H}_2\bar{\text{T}}$  or .188 of  $\text{KHT}$ .

b. Another portion of the sample (2 grammes) is calcined in platinum at a very low red heat.\* The ash is dissolved in hot water, and, without filtration, treated with a moderate excess of standard acid, and the solution boiled. The excess of acid is then ascertained by titrating back with standard alkali. From the alkalinity of the tartar after ignition is subtracted the alkali required to neutralise an equal weight of the original tartar, both expressed in terms of normal alkali, when the difference is the neutralising power of the bases existing as neutral tartrates. 1 c.c. of normal alkali is equivalent to .1131 grammes of  $\text{K}_2\bar{\text{T}}$ , .104 grammes of  $\text{Ca}\bar{\text{T}}$ , or .750 grammes of  $\text{H}_2\bar{\text{T}}$  as a neutral tartrate.

A preferable, but somewhat more tedious method for the assay of lees and argol, is the direct estimation of the tartaric acid by precipitation as  $\text{KHT}$ , after previous decomposition of calcium tartrate by oxalate of potassium. The following are the details recommended by Mr Warington:†—

An amount of the powdered sample containing about 2 grammes of tartaric acid is placed in a beaker, and heated with a small quantity of water till thoroughly softened. A strong solution of neutral potassium oxalate is next added in quantity sufficient to react with all the calcium salts present, and leave an excess of about  $1\frac{1}{2}$  grammes of the salt. The mixture is heated, with frequent stirring for some time longer. The solution, which will generally be strongly acid, is now cautiously treated with solution of pure potash till almost neutral. After a little further heating, the liquid (which should not occupy more than 40 c.c.) is filtered on to a small filter. The residue is well washed, the washings concentrated on the water-bath, and added to the main solution, which is made up

\* Complete combustion of the carbon is not to be expected. If the sample contained sulphates, 5 c.c. of solution of hydrogen dioxide should be added to the solution of the ash immediately prior to the standard acid.

† *Journ. Chem. Soc.* 1875, page 973.

to about 50 c.c. A strong solution of about 2 grammes of citric acid is next added, and the solution well stirred to facilitate precipitation of the  $\text{KHT}$ . After twelve hours, the precipitate is collected on a small filter, washed with a saturated solution of acid potassium tartrate containing 5 per cent. of potassium chloride, the filter and contents removed to a beaker, treated with hot water, and titrated with standard alkali. Each c.c. of normal alkali equals .150 grammes of  $\text{H}_2\text{T}$ .\*

This direct method of determining tartaric acid in tartars, &c., gives results somewhat lower than those obtained by the indirect alkalimetric method, but they are more accurate and consistent with results of the factory.

**Calcium Tartrate**,  $\text{CaC}_4\text{H}_4\text{O}_6 = \text{CaT}$ , is a natural constituent of the tartarous deposit from wine, the proportion contained being much increased if the wine has been "plastered." (See page 253.) It also constitutes the greater part of the residue obtained on treating commercial tartars with hot water. Tartrate of calcium is also precipitated as a crystalline powder containing  $4\text{H}_2\text{O}$ , by adding excess of calcium chloride to a solution of a neutral tartrate. It is soluble in 6265 parts of water at  $15^\circ \text{C}$ . ( $=59^\circ \text{F}$ .), and in 352 parts of boiling water. Free acids and cream of tartar dissolve it readily. (Hence its presence even in purified tartars.) The solutions are precipitated by ammonia, either immediately or after some time. Calcium tartrate is soluble in ammonium chloride and in cold caustic alkali; the latter solution is reprecipitated on boiling. By digestion with a hot neutral solution of cupric chloride it is converted into insoluble cupric tartrate. This reaction distinguishes it from

\* A test experiment should be first made on a known quantity of tartaric acid or a pure tartrate, and a correction based on the result obtained should be applied for  $\text{KHT}$  left in permanent solution, less that retained in the form of wash water. Thus the amount of  $\text{KHT}$  dissolved will probably be about .06 grammes, or 3 per cent. of the tartaric acid found; but this will be decreased by the amount of  $\text{KHT}$  contained in the wash-water retained by the filter. This will depend on the size of the filter and precipitate.



calcium citrate. It differs from the racemate and oxalate of calcium by its solubility in acetic acid.

Moist tartrate of calcium, if kept warm, undergoes fermentation and forms butyrate of calcium.

The ACID TARTRATE OF CALCIUM is sparingly soluble; in solution it is unstable, the liquid gradually depositing crystals of the neutral salt.

For further information on tartrate of calcium and methods of determining it in tartarous deposits, see the articles on lees, tartar, &c., page 253, *et seq.*

**Cupric Tartrate**,  $\text{Cu}^{\text{II}}\bar{\text{T}}$ , is an almost insoluble blue crystalline powder, prepared by precipitating a neutral soluble tartrate by neutral sulphate or chloride of copper. It is of interest as affording a means of separating tartrates from citrates, the citrate of copper being soluble. (See pages 248, 256, and 262). Cupric tartrate is soluble in ammonia, soda, and potash. The two last solutions are frequently employed for the detection of glucose and inverted sugar, being usually known as:—

FEHLING'S SOLUTION OR TRÖMMER'S TEST. This reagent ought always to be tested before being used, by adding an equal bulk of water and heating to boiling for a few minutes, when it should remain perfectly clear; old Fehling's solution may often be made usable by addition of more alkali. According to Boussingault, when prepared in the following manner, the solution is not liable to change:—Dissolve 40 grammes of crystallised cupric sulphate in 200 c.c. of water; take 160 grammes of neutral potassium tartrate and 130 grammes of fused sodium hydrate, and dissolve in 600 c.c. of water. Mix the two solutions, dilute to 1 litre, and boil for some minutes.

Fehling's solution gives a yellow or red precipitate of cuprous oxide,  $\text{Cu}_2\text{O}$ , when heated nearly to boiling with dextrose, lævulose, maltose, lactose, dextrin, aldehyde, chloral, pyrogallie acid, gallotannic acid, or arsenious acid.



It is not reduced when heated nearly to boiling with cane-sugar, gum-arabic, alcohol, acetic acid, oxalic acid, tartaric acid, citric acid, gallic acid, glycerin, urea, uric acid, &c.

**Potassium-hydrogen Tartrate;** Acid potassium tartrate; Bitartrate of potassium; Cream of tartar.  $\text{KH},\text{C}_4\text{H}_4\text{O}_6=\text{KHT}$ . —This substance is the principal constituent of tartar, argol, and wine-lees, and is of importance in the free state as a source of tartaric acid, and as a form for the determination of that body.

Acid tartrate of potassium is a white substance forming hard, trimetric crystals. It is soluble in 240 parts of water at  $10^\circ\text{C}$ . ( $=50^\circ\text{F}$ .), 180 at  $20^\circ\text{C}$ ., and in about 15 parts of boiling water. In alcoholic liquors it is much less soluble. Thus it requires (at  $15^\circ\text{C}$ .) 400 parts of a spirit containing 10·5 per cent. of alcohol, and 2000 parts of proof spirit (49·24 per cent. alcohol) for solution. In still stronger spirit it is practically insoluble. The presence of glucose does not affect its solubility in water or weak spirit; but the presence of certain salts and acids has great influence. This is shown by the following table by Warington, in which the effect of water containing equivalent\* quantities of various acids is given. For comparison with them, experiments were also made with solutions containing equivalent amounts of acetic and citric acids neutralised by potash. All the experiments were made at  $14^\circ\text{C}$ .:—

Solvent.	Grammes of Acid or Salt in 100 c.c. of Solvent.	Grammes of KHT Dissolved by 100 c.c. of Solvent.
Water . . . . .	—	·422
Acetic acid . . . . .	·8106	·422
Tartaric acid . . . . .	1·0331	·322
Citric acid . . . . .	·8448	·546
Sulphuric acid . . . . .	·6853	1·701
Hydrochloric acid . . . . .	·5037	1·949
Nitric acid . . . . .	·8445	1·969
Potassium acetate . . . . .	1·3875	·744
Potassium citrate . . . . .	1·3966	·843

\* Not equal weights, but amounts of acid requiring equal quantities of alkali for their neutralisation.

These results are of importance in the estimation of tartaric acid as  $\text{KHT}$ . Clearly free mineral acids should not be present, nor any large excess of potassium acetate or citrate. On the other hand, solutions of the sulphate, nitrate, and especially the chloride of potassium, have very little solvent action on the precipitated acid tartrate.

Commercial cream of tartar usually contains a small proportion of calcium tartrate. For its examination and assay, see the article on "tartar," page 253.

Acid tartrate of potassium dissolves many metallic oxides, forming double tartrates; tartar-emetic,  $\text{K}(\text{SbO})\bar{\text{T}}$ , is a compound of this character.

When cream of tartar is treated with solution of potash till the liquid ceases to redden litmus paper, there results:—

**Neutral Potassium Tartrate;** Di-potassium tartrate.  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6 = \text{K}_2\bar{\text{T}}$ .—This forms *very soluble* monoclinic prisms. When its solution is treated with an acid,  $\text{KHT}$  is precipitated.

**Potassium-sodium Tartrate,** or Rochelle salt,  $\text{KNa}\bar{\text{T}}$ , is produced by neutralising cream of tartar with soda or sodium carbonate. It forms large rhombic prisms, containing four atoms of water, and is very readily soluble. Addition of acetic acid precipitates crystalline  $\text{KHT}$ . This reaction distinguishes it from the neutral sodium tartrate,  $\text{Na}_2\bar{\text{T}} + 2\text{H}_2\text{O}$ .

**Potassium-ferric Tartrate;** Potassio-tartrate of iron,  $\text{K}_3\text{Fe}'''\bar{\text{T}}_3$ .—Prepared by adding precipitated ferric hydrate to cream of tartar, and then treating with cold water. It constitutes the *Ferrum Tartaratum* of Pharmacy. The solution acidulated with hydrochloric acid should give a copious blue precipitate with the ferrocyanide, but none with the ferricyanide of potassium. It should contain 30 per cent. of  $\text{Fe}_2\text{O}_3$ , as estimated from the weight of the ash insoluble in water.

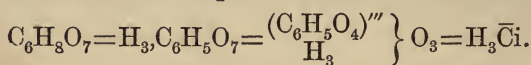
**Potassium Antimony Tartrate;** Tartarised Antimony; Tartar-emetic. French—*Tartre Stibié*.  $\text{K}(\text{SbO})'\text{C}_4\text{H}_4\text{O}_6$ .—This important remedy is prepared by mixing antimonious oxide ( $\text{Sb}_2\text{O}_3$ ) with cream of tartar, and subsequently adding

water, boiling, filtering, and crystallising. The crystals contain half an atom of water. Cold water dissolves 7 per cent., and boiling water 53 per cent. of the salt; the solution has an acid reaction. The salt is little liable to adulteration. "Antimonial wine" is an official solution of 40 grains of tartar-emetic in a pint of sherry.

**The Tartrates of Ammonium** closely resemble the corresponding potassium salts, but are wholly volatile on ignition.

### CITRIC ACID.

*French*—Acide Citrique. *German*—Citronsäure.



Citric acid occurs in a free state in the juice of the whole genus of plants *Citrus* (order, *Aurantiaceæ*), and also in the gooseberry, cranberry, currant, tamarind, and many other fruits. The lemon, lime, and bergamot are the fruits from which it is extracted. It has also been manufactured from unripe gooseberries, which yield about 1 per cent. of their weight. Good lemons yield about  $5\frac{1}{2}$  per cent. of crystallised acid.

Citric acid usually occurs as a crystalline powder, or in transparent colourless prisms belonging to the trimetric system. It readily crystallises from a hot aqueous solution. In the trade, citric acid crystals are always assumed to have the composition  $2\text{C}_6\text{H}_8\text{O}_7 + \text{H}_2\text{O}$ , but seventeen samples from various makers were found by Warington to contain from 8.46 to 9.35 per cent. of water, the average being 8.72 per cent. This result agrees with the formula  $\text{C}_6\text{H}_8\text{O}_7 + \text{H}_2\text{O}$ , which requires 8.57 per cent. of water.

In determining the water in citric acid, it is necessary to dry the powdered sample for some hours at  $50^\circ$  to  $60^\circ$  C., and then gradually to raise the temperature to  $100^\circ$  C. Some samples lose their water much more readily than others; many samples effloresce in warm dry air.

Citric acid has a strong, but pleasant acid taste. Four parts of citric acid dissolve in three parts of cold, or two of boiling water. The solution has no rotatory action on a ray of light.

Aqueous solutions of citric acid readily turn mouldy. When mixed with chalk and yeast, and exposed to a temperature of about  $25^{\circ}\text{C}$ ., the solution ferments, with formation of acetate and butyrate of calcium.

Citric acid is soluble in aqueous and in absolute alcohol, but is nearly insoluble in ether.

When heated with concentrated sulphuric acid, citric acid turns brown, and gives off carbonic oxide, acetone, and other products. Heated with an alkali, it yields an oxalate and acetate. When heated alone, citric acid melts in its water of crystallisation, and at a higher temperature is converted into a conitic acid,  $\text{C}_6\text{H}_6\text{O}_6$ , and ultimately into other products. The charcoal which is the ultimate product of its decomposition is readily combustible.

DETECTION AND DETERMINATION OF CITRIC ACID AND CITRATES.—When 5 grammes of citric acid are heated with 30 c.c. of ammonia for six hours in a sealed tube at a temperature of  $120^{\circ}\text{C}$ .,\* a yellow coloration is observed, and small crystals are formed. If the cooled liquid be poured into an evaporating basin, it becomes blue in the course of some hours, the colour becoming more intense on standing, and in a few days turning to green, and ultimately disappearing. The change of colour goes on more slowly in the dark. Heating the liquid on the water bath hastens the production of the colour. Malic, tartaric, and oxalic acids do not interfere, even when present in large excess; but itaconic acid must be absent. It is said that 0.01 grammes of citric acid can be detected by this process.†

Citric acid contains three atoms of replaceable hydrogen,

\* This temperature is conveniently obtained by immersing the tube in a bath of boiling saturated solution of nitrate of sodium.

† Sabanin and Laskowsky, *Zeitsch. Anal. Chem.*, xvii. 73, and *Journ. Chem. Soc.* April, 1878. I have no experience of this test.



and therefore forms three classes of citrates. It has a great tendency to produce stable double citrates, and hence many metallic solutions are not precipitable by alkalis in presence of sufficient citric acid. This fact is often utilised in analysis.

None of the citrates are completely insoluble in water. The citrate of calcium is very sparingly soluble, and less soluble in hot water than in cold. Hence, addition of excess of lime water to a solution of citric acid produces but a slight precipitate in the cold, but a somewhat more considerable precipitate of tricalcic citrate,  $\text{Ca}_3\overline{\text{Ci}}_2$ , is obtained on boiling, the deposit redissolving as the solution cools.

Precipitation as tricalcic citrate serves to separate citrates from malates, acetates, formates, butyrates, &c.

From oxalic acid citric acid is separated by neutralising the solution with soda, acidifying with acetic acid, and adding calcium sulphate or chloride. After filtering from the precipitated calcium oxalate, the citric acid may be thrown down by adding lime water and boiling, or as described on page 268.

From tartaric acid, citric acid is separated by the method described on page 264. In the filtrate from the precipitate of acid potassium tartrate, the citric acid may be determined by boiling off the alcohol, exactly neutralising with soda, and proceeding as directed on page 268, or by precipitation with barium acetate or lead acetate (page 263). If the acids do not exist in the free state, the solution must be prepared as directed under tartaric acid (see page 248).

Citric acid may also be separated from tartaric acid by digesting the mixed calcium salts with a hot solution of perfectly neutral cupric chloride,\* when soluble cupric citrate is formed, and an insoluble tartrate remains. In

\* This solution is best extemporised by precipitating a solution of cupric sulphate by barium chloride, and filtering from the resultant sulphate of barium.

the case of mixed tartrates and citrates which can be converted into the calcium salts by precipitation with calcium chloride or nitrate in perfectly neutral boiling solution, this method of separation is very convenient.

In the absence of other free acids, citric acid can be determined by titration with standard alkali, but as it gives no sharp reaction with either logwood, cochineal, or litmus, the end of the reaction is very difficult to observe, and the change of colour is often very gradual. Carefully made litmus paper is preferable to the solution, and the alkali should be caustic soda prepared from sodium. A decinormal solution may be used, but its neutralising power should be ascertained by titration with pure citric acid, as the change of reddened litmus to blue occurs somewhat before sufficient soda has been added to form  $\text{Na}_3\text{Ci}$ . For this purpose the crystallised acid should be powdered, water determined in one portion (see page 260), and a titration made with soda and litmus in another portion. Full descriptions of the methods employed for determining citric acid in lemon juice, citric acid liquors, &c., are given under their respective heads (see page 266, *et seq.*).

Citric acid may also be determined by precipitation as a calcium salt, as described on page 268. If moderately pure, it may also be converted into barium citrate by precipitating the neutralised solution with barium acetate, and adding two volumes of 95 per cent. alcohol. After twenty-four hours, the precipitate is filtered off, washed with alcohol of 63 per cent., ignited, moistened with sulphuric acid, again ignited, and a weight multiplied by 0.601. Alkaline acetates do not interfere, so that the method is applicable to liquids from which the tartaric acid has been separated as  $\text{KHT}$ .

For the estimation of citric acid in presence of heavy metals the latter are first removed by sulphuretted hydrogen or sulphide of sodium, and the filtered liquid rendered neutral and precipitated with excess of lead. The liquid is mixed with an equal volume of alcohol, filtered, the precipitate washed with

proof-spirit, and treated with ammonia. The filtrate may contain citric and tartaric acids, but will be free from sulphates, phosphates, and oxalates. When unmixed with other lead salts, citrate of lead may be suspended in water, decomposed by sulphuretted hydrogen, the liquid filtered, well boiled, and the free citric acid in the solution titrated with standard alkali.

**Commercial Citric Acid** frequently contains small quantities of calcium salts, due to imperfect manufacture, and traces of iron, lead, and copper are also met with—these last being derived from the vessels used for the crystallisation and evaporation of the acid liquids.

The presence of all these impurities is indicated by igniting five or ten grammes of the sample in a porcelain crucible. The ash usually varies from 0.05 to 0.25 per cent. When the proportion of ash does not exceed the latter amount, it is rarely of importance to examine it further, except for poisonous metals. The presence of lead or copper will be readily indicated by dissolving the ash in a few drops of nitric acid, diluting largely, and passing sulphuretted hydrogen.

A very fair approximative determination of the lead or copper present may be obtained by placing the solution of the ash in a tall glass cylinder or white porcelain basin, and comparing the depth of tint produced by sulphuretted hydrogen with that obtained by treating an equal bulk of a very weak standard solution of lead or copper in a similar manner.\* If the metal present be copper, a blue colour will be observed on treating the ash with nitric acid, and the diluted solution will give a brown colour with potassium ferrocyanide.

The presence of poisonous metals in citric acid is always accidental; but as lead and copper are occasionally present in dangerous amount, it is necessary to take every precaution to avoid their introduction.

\* This method is almost identical with that used by Wanklyn for the estimation of copper or lead in drinking water, but for the sulphide of ammonium recommended by him sulphuretted hydrogen is necessarily substituted. The same method can be satisfactorily applied to the direct determination of lead in lemonade and other aerated waters.



Many samples of citric acid contain free sulphuric acid, an impurity which renders the crystals deliquescent. Sulphuric acid and sulphates may be detected and estimated by acidifying rather strongly with hydrochloric acid and adding barium chloride. 233 parts of the white precipitate of  $\text{BaSO}_4$  correspond to 98 of sulphuric acid ( $\text{H}_2\text{SO}_4$ ).

The most common adulterant of citric acid, and almost the only substance purposely mixed with it, is tartaric acid,\* which can be detected and estimated by converting it into the nearly insoluble acid tartrate of potassium, according to the following method:—

Two grammes of the sample of acid are dissolved in 20 c.c. of proof-spirit (made by diluting methylated spirit to a density of .920), the solution filtered from any residue (consisting of tartrates of potassium and calcium, &c.), and made up to 45 c.c. with proof-spirit. 5 c.c. of a cold saturated solution of potassium acetate in proof-spirit are next added, the liquid well stirred, and allowed to stand for twelve hours. If any tartaric acid be present it will be thrown down as a crystalline precipitate of  $\text{KH}_2\text{C}_4\text{H}_4\text{O}_6$ . When the proportion is very small there may be no defined precipitate, but there will be white streaks on the sides of the vessel, in the track of the glass rod used for stirring. Two per cent. of tartaric acid in samples of citric acid can thus be detected. When more than a trace of precipitate is obtained, it is filtered off and washed with proof-spirit. Rinse the precipitate from the filter with a saturated solution of potassium-hydrogen tartrate in cold water,† digest

\* The tests for tartaric acid with chloride of calcium, alkaline permanganate, and ferric hydrate, have not in my hands given satisfactory results, either qualitative or quantitative. The details of the method here given are those published by me in a paper on "The Adulterations and Impurities of Tartaric and Citric Acids."—*Chem. News*, 1875, vol. xxxi. p. 277.

† This is necessary to get rid of any co-precipitated citrate, which in the concentrated spirituous solutions employed has a great tendency to be dragged down with the tartrate. In cold weather a very copious precipitation of an acid potassium citrate sometimes occurs, but it dissolves with facility when digested with the solution of acid tartrate of potassium.



in the cold for a few hours, with occasional stirring, filter, and wash once with proof-spirit. The precipitate consists of potassium-hydrogen tartrate. It may be rinsed off the filter with boiling water into a small porcelain dish, and weighed after evaporating off the water at  $100^{\circ}\text{C.}$  ( $=212^{\circ}\text{F.}$ ). The weight multiplied by the factor 0.798 (or roughly, 0.8) gives the quantity of tartaric acid in 2 grammes of the sample taken. Instead of weighing the precipitate, it may be dissolved in hot water and titrated with standard alkali and litmus in the ordinary manner, when each c.c. of normal alkali used equals 0.150 grammes of tartaric acid in the 2 grammes of sample taken.\* In many respects this method is preferable to the actual weighing of the precipitate. When great accuracy is desired, a correction should be made for the solubility of the precipitate in the mother-liquor. When the foregoing directions are adhered to, an addition of 0.020 grammes to the weight of tartaric acid actually found is sufficiently near the truth. If desired, the citric acid may be determined in the filtrate. See page 262.

**Lemon-juice; Bergamot-juice; Lime-juice.**—These juices contain free citric acid, free acids other than citric, citrates, salts of organic acids other than citric, salts of inorganic acids, albuminous, mucilaginous, saccharine and other indifferent bodies. Spirit is frequently added as a preservative, and mineral acids are not uncommonly employed as adulterants. Verjuice has also been used for the purpose.

THE ASSAY OF GENUINE JUICE is practically confined to the determination of citric acid and citrates, and for this purpose the following processes are employed:—

*a. Determination of the specific gravity.* A special hydrometer is sometimes used. On this “citrometer,”  $60^{\circ}$  corre-

\* A method closely resembling the above has been described by E. Fleischer, but by strictly following his directions I obtained a precipitate containing a considerable admixture of citrate. See also the article on “tartaric acid,” page 246.

spend to 1.24 specific gravity, so that each degree appears to be equal to 0.004 specific gravity.

The valuation by specific gravity is open to many frauds. Bergamot-juice, which has a high gravity but low acidity, has been mixed with lemon-juice, and sea-water has been added to the juice during concentration. Of course the presence of alcohol materially affects the density, but its influence may be got rid of by boiling the juice and again taking the density after making up the volume to that originally employed.

*b. Determination of the free acid.* This is effected by titration with decinormal caustic soda, as described on page 262. In the case of concentrated juice, 50 c.c. should be diluted to 500, and 25 c.c. to 30 c.c. of the diluted liquid employed for the titration. With unconcentrated juice, 10 c.c. or 20 c.c. may be measured out at once. In either case, the alkali is added in quantity sufficient to neutralise about  $\frac{5}{6}$ ths of the acid present; the liquid is then boiled for a few minutes, and when quite cold the titration is completed. The neutralising power of the alkali should be known in terms of pure citric acid. Owing to the want of sharpness in the reaction of citric acid with litmus-paper, the determination does not admit of great accuracy. Experiments with concentrated juice will not agree nearer than  $\frac{1}{4}$  oz. of citric acid per gallon. The number of grammes of citric acid contained in each c.c. of the juice, multiplied by 160, gives the ounces of acid per gallon.

*c. Determination of the citric and other organic acids in combination with bases.* This is effected by evaporating to dryness the portion of juice which has been already neutralised by soda for the determination of the free acid. The residue left on evaporation is heated gradually, and charred at a low red heat. The ignited mass is treated with water, a known volume of standard sulphuric acid added, the liquid boiled and filtered, and the excess of sulphuric acid determined in the filtrate by standard alkali. The amount of sulphuric acid neutralised by the ash is equivalent to the total organic acid

of the sample, for on ignition all the salts of organic acids were converted into the corresponding carbonates. 49 parts of  $\text{H}_2\text{SO}_4$  neutralised = 40 of  $\text{NaHO}$  = 70 of  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$  or 67 of  $2\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ .

This, then, gives the total organic acid of the juice taken, calculated as citric acid. By subtracting the amount of free citric acid obtained by titration of the acid juice, the amount of combined citric acid is ascertained.

If the original acid juice be evaporated and ignited, and the combined citric acid calculated from the neutralising power of the ash, the results obtained are too high, owing to the decomposition of chlorides, &c., by the citric acid during evaporation.

*d. Determination of the real citric acid.* Of the organic acids present in genuine lemon and similar juices, the citric is the only one of importance which forms an approximately insoluble calcium salt. Malate and aconitate of calcium are pretty freely soluble, and the same remark applies more strongly to the acetate and butyrate of calcium produced by the fermentation of citric acid juices. For the determination of the amount of insoluble calcium salt obtainable from a juice, Mr R. Warington recommends the following method: \*— 15 to 20 c.c. of unconcentrated lemon-juice, or about 3 c.c. of concentrated juice (previously diluted to facilitate exact measurement), are exactly neutralised with pure caustic soda. The solution is brought to a bulk of about 50 c.c., and heated to boiling in a salt-bath, and so much of a solution of calcium chloride added as is known to be rather more than equivalent to the total organic acids present. The whole is boiled for half an hour, and the precipitate then collected and washed with hot water. The filtrate and washings are concentrated to

\* *Journ. Chem. Soc.* 1875, page 934. Had the analytical examination of other organic products been worked out so exhaustively as those of the citric acid manufacture have been by Mr Warington, this book would never have been written. Almost the whole of the information given under the head of citric acid is culled from Mr Warington's admirable paper.



about 10 or 15 c.c., the solution being finally neutralised with a drop of ammonia if it has become acid. The second precipitate thus obtained is collected on a very small filter, the filtrate being employed to transfer it and the washing with hot water being reduced as much as possible. The precipitates, with their filters, are then burnt at a low red heat, and the neutralising power of the ash ascertained by treatment with standard acid (HCl is preferable) and alkali. Each c.c. of normal acid neutralised corresponds to 0.070 grammes of crystallised citric acid ( $\text{H}_3\bar{\text{C}}\text{i} + \text{H}_2\text{O}$ ). The presence of mineral acids does not interfere; oxalic or tartaric acid would render the results inaccurate.

In English-pressed lemon-juice the real citric acid is 99 per cent. of the total organic acid, but in the concentrated Sicilian juice it varies from 88 to 95 per cent. of the total. In a sample of concentrated bergamot-juice, Warington found the precipitated acid to be about 88 per cent. of the total organic acid, but a more usual proportion is 96 to 98 per cent. The method of determining the value of juice by its acidity gives tolerably accurate results in the case of lemon and bergamot juice, but in lime-juice the results are in excess of the truth. Of course this remark is only true of genuine juice.

*e. Determination of alcohol.* This can be effected by the ordinary distillation method described on page 94.

A very pure preparation has been introduced by the Montserrat Lime Juice Company. The producers grow their own limes on the Island of Montserrat, and by care in the preparation of the juice, and proper precautions to avoid fermentation, they obtain and export a very superior product.

Citric acid juices lose some of their acidity by concentration. Warington observed a loss of 3.5 per cent. of the total free acid on concentrating English-pressed juice to one-sixth of its original bulk. The loss is due, at least in part, to the presence of volatile organic acids, which, of course, exist in much smaller amount in concentrated juice. Warington found



1·25 per cent. of the total acidity of concentrated juice to be due to volatile acids. Among the latter were recognised formic, acetic, and probably propionic acids.

The following table shows the density, free acid, and combined organic acid (the two last expressed in terms of crystallised citric acid,  $\text{H}_3\bar{\text{C}}\text{i}, \text{H}_2\text{O}$ ) of the various citric juices commonly met with in commerce:—

	Density.	Free Acid. oz. per gallon.	Combined Organic Acid. oz. per gallon.
<i>Lemon-juice—</i>			
Raw Sicilian . .	...	6-9	0·85
„ English . .	1·04-1·05	11-13	0·3
Concentrated . .	1·20-1·25	56-72	6-8
<i>Bergamot-juice—</i>			
Concentrated . .	1·22-1·25	47-55	7-8
<i>Lime-juice—</i>			
Raw . . . .	1·035-1·040	10·6-13·5	0·4-0·7
Concentrated . .	1·28 -1·38	82-112	8·6

From this table it will be seen that English-pressed juice contains more free and less combined acid than the raw Italian and Sicilian juice. This is probably due to the fact that the finest and ripest fruit is sent to England, while the windfalls and damaged fruits are treated locally. Concentrated lemon-juice is considered of standard quality when it contains free acid equal to 66·87 of crystallised citric acid ( $\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$ ) or 64 oz. of nominal acid ( $2\text{H}_3\bar{\text{C}}\text{i} + \text{H}_2\text{O}$ ). The Board of Trade standard for lemon-juice is a density of 1·030 (without spirit), and an acidity equivalent to 30 grains per ounce (=11 ounces per gallon) of citric acid.

According to the British Pharmacopœia, lemon-juice should have a density of 1·039, and should contain  $32\frac{1}{2}$  grains of acid per ounce (=11·9 ounces per gallon).\*

Concentrated bergamot-juice is far less acid than lemon-juice, while concentrated lime-juice is a thick viscid fluid far exceeding the others both in density and acidity.

\* According to Stoddart, this density is too high for the proportion of acid.

Lemon- and lime-juices are extensively employed as anti-scorbutics. The ash of lemon-juice has been found to contain 54 per cent. of potash and 15 per cent. of phosphoric acid; but as the proportion of mineral matter is very small, it is difficult to attribute the effects of lemon-juice to the constituents of the ash.

ADULTERATED LIME- AND LEMON-JUICES are not uncommon. The production of considerable precipitates with barium chloride and silver nitrate sufficiently indicates the presence of sulphuric and hydrochloric acids respectively, pure juices containing merely insignificant traces of sulphates and chlorides.\* Free sulphuric acid may also be determined as in citric acid liquors (see page 272), and both that and free hydrochloric acid by Hehner's method for the determination of mineral acids in vinegar (page 199).

According to F. D. Scribani,† nitric acid has recently come into use for the adulteration of lemon-juice. On concentrating such juice the nitric acid decomposes the citric acid, either wholly or partially, with formation of oxalic, acetic, and carbonic acids; so that on neutralising the juice with lime a mixture of calcium salts is obtained. To detect the nitric acid, Scribani adds to the juice an aqueous solution of ferrous chloride, strongly acidulated with pure hydrochloric acid and quite free from ferric salt. The liquid is then boiled for a few minutes, and, after cooling, tested with a thiocyanate (sulphocyanide). If the liquid contain nitric acid, a more or less deep-red colour will be produced, owing to the formation of a ferric salt. This test is said to answer equally well in presence of common salt or sulphuric or tartaric acid.‡ In boiled and dark-coloured juices dilution is necessary before the colour can be observed.

\* Sea water has been added to lemon-juice, and would, of course, react with silver nitrate.

† *Gaz. Chim. Ital.* viii. 284, and *Journ. Chem. Soc.* ii. 1878, page 914.

‡ A more satisfactory and direct test for nitric acid would be to boil the juice with metallic copper, when red fumes will be produced if nitric acid be present.

**Citric Acid Liquors.**—This term is applied to the liquors resulting in citric acid works from the treatment of the citrate of calcium with sulphuric acid. Their assay is limited to the determination of the contained citric and sulphuric acids. For this purpose the total acidity may be determined by titration (see page 267), and the free sulphuric acid then estimated. By subtracting the acidity due to the latter from the total found by titration, that due to the citric acid alone is ascertained. The free sulphuric acid is determined by treating 10 or 20 c.c. of the liquor with five times its volume of strong alcohol. After twelve hours, a portion of the clear liquor is treated with more alcohol, and, if opalescence result, the whole is treated in the same way. The liquid is ultimately filtered, the precipitated sulphates washed with spirit, and the filtrate precipitated with an alcoholic solution of calcium chloride. The precipitated calcium sulphate is allowed to settle completely, the supernatant liquor poured off, and the precipitate and small quantity of remaining liquor *gently warmed*. The alcohol is gradually displaced by cautious additions of small quantities of water, and, when the precipitate has become crystalline from its conversion into gypsum, alcohol is added, and the precipitate collected on a filter, washed with spirit, ignited, and weighed as  $\text{CaSO}_4$ . The weight multiplied by .7206 gives the sulphuric acid ( $\text{H}_2\text{SO}_4$ ) in the liquor taken.

Another method, which agrees well with the last, is to neutralise exactly a known measure of the liquor with pure caustic soda, evaporate to dryness, and ignite gently in platinum. The ash is wholly dissolved in a known quantity of standard acid, and the excess of acid ascertained by titration with alkali. (In presence of iron or aluminium, some neutral sodium tartrate or Rochelle salt should be added before titration.) The acid neutralised by the ash is equivalent to the organic acid contained in the liquor used.

In old liquor, the citric acid should be precipitated as calcium salt, as other organic acids will be present in serious amount.



For this purpose, the liquor is treated exactly as directed for juice on page 268.

**Calcium Citrate.**  $\text{Ca}_3\text{C}_{12}\text{H}_{10}\text{O}_{14} = \text{Ca}_3\overline{\text{Ci}}_2$ .—This is a white substance, very sparingly soluble in cold, and still less in hot water. It is produced, in an impure state, by the citric acid manufacturer by boiling the juice with chalk, and is sometimes offered in the market as a convenient source of citric acid. The product consists essentially of citrate mixed with other salts of calcium, and excess of chalk or lime. In Sicily, dolomitic lime is sometimes used for neutralising the juice, in which case magnesium salts will be present. It is particularly liable to decompose if the percentage of moisture is considerable (more than 10 or 12 per cent.), and therefore some samples contain scarcely any real citrate. For the analytical examination of commercial citrate of calcium, it is sufficient to determine the citric acid and the excess of chalk or lime. For the latter purpose, 5 grammes of the sample should be dissolved in a known quantity of weak standard hydrochloric acid kept gently boiling, and, when the solution is quite cold, the amount of acid neutralised is ascertained by titration with standard alkali, as described on page 266. Each c.c. of normal acid neutralised by the sample corresponds to 0.050 grammes of chalk in the portion taken. To determine the organic acids, 2 grammes of the sample are ignited, the ash boiled with standard HCl, the liquid filtered and titrated with alkali. The acid neutralised by the ash is due to the chalk existing as such in the sample, *plus* the calcium carbonate produced by the ignition of the citrate and other organic salts. By subtracting the neutralisation due to the chalk proper, the equivalent of the organic acids is found; each c.c. of normal HCl neutralised being equivalent to .070 grammes of  $\text{H}_3\overline{\text{Ci}}, \text{H}_2\text{O}$ . This method gives all the organic acids as citric acid, a result which is misleading in decomposed citrate. In such samples, the real citric acid should be determined by dissolving a known weight in hydrochloric acid, exactly neutralising with caustic soda, and



treating the precipitated citrate of calcium as described on page 268. Citrate of magnesium, or citrate prepared with dolomitic lime, can be correctly analysed by the titration method; but if precipitation be desired, the sample must be decomposed by boiling with carbonate of sodium, the carbonate of magnesium filtered off, the filtrate neutralised with hydrochloric acid, and precipitated with calcium chloride as described on page 268.

**Lithium Citrate.**  $\text{Li}_3\text{Ci}$ .—As usually prepared, this is a white powder, but it may be obtained in crystals with 4Aq. The salt is generally stated to be deliquescent, but this is an error. It should be soluble without residue in twenty-five parts of cold water.

The pure salt, after being rendered anhydrous by drying at  $115^\circ \text{C}$ ., on ignition leaves 52.9 per cent. of lithium carbonate,  $\text{LiCO}_3$ . The residue should be treated with ammonium carbonate, and again ignited very gently, as it is liable to lose carbonic acid. A higher ash than the above indicates impurity or adulteration by (probably) sodium citrate, which leaves 61.5 per cent. on ignition. One gramme of anhydrous lithium citrate leaves on ignition a residue which should neutralise at least 14 c.c. of normal acid. The same amount of sodium citrate (after ignition) would only neutralise 11.25 of acid.

Much of the commercial lithium citrate contains lithium carbonate. This gives it an alkaline reaction, and increases its ash *and* its saturating power. Excess of citric acid gives the salt an acid reaction, and reduces the percentage of ash *and* the saturating power. Hence these impurities can be distinguished from sodium citrate, which *raises* the ash and *diminishes* the saturating power of the sample.

**Magnesium Citrate** is an intermediate form into which the citric acid of lemon juice is sometimes converted. The popular medicine known as “Effervescent Citrate of Magnesia,” is a mixture of citric and tartaric acids with acid carbonate of sodium, loaf sugar, and about 3

per cent. of crystallised magnesium sulphate. The last constituent and the citric acid are frequently omitted.

**Citrate of Iron and Ammonium.**—An official preparation made by dissolving precipitated ferric hydrate in citric acid, and adding ammonia. It occurs in thin transparent scales of a deep red colour and slightly sweetish and astringent taste. Heated with solution of caustic potash (*not* soda) its solution evolves ammonia and deposits ferric hydrate; the alkaline solution filtered from the iron should not give any crystalline precipitate (or streaks) of  $\text{KHT}$  when acidulated with acetic acid and vigorously stirred. Ignited in the air, the official preparation should leave not less than 27 per cent. of  $\text{Fe}_2\text{O}_3$ , free from alkaline reaction when moistened. Citrate of iron and ammonium is readily soluble in water (forming a faintly acid solution), but it is almost insoluble in rectified spirit. A solution of 160 grains in one pint of orange wine forms the *Vinum Ferri Citras* of the Pharmacopœia.

**Citrate of Iron and Quinine.**—This preparation will be described in connection with other preparations of quinine.

**Citrate of Bismuth and Ammonium** is a convenient form for administering bismuth, as its solution is not precipitated by dilution with water. The official "*Liquor*" has a density of 1.122, and contains 24 grains of  $\text{Bi}_2\text{O}_3$  to the fluid ounce. The bismuth is best determined by precipitation of the diluted liquid with sulphuretted hydrogen; 1 fluid ounce should yield 26.48 grains of  $\text{Bi}_2\text{S}_3$ .

**Aconitic Acid;**  $\text{C}_6\text{H}_6\text{O}_6 = \text{H}_3\text{C}_6\text{H}_3\text{O}_6 = \left. \begin{matrix} \text{C}_6\text{H}_3\text{O}_3 \\ \text{H}_3 \end{matrix} \right\} \text{O}_3$ .—This is an unimportant acid contained as a calcium salt in *Aconitum napellus*, and several plants of the same genus. It also exists as a magnesium salt in *Equisetum fluviatile*, and is a product of the dehydration of citric acid (see page 261). It is occasionally present in citric acid liquors, and has been found in concentrated cane-juice from the West Indies.

Aconitic acid crystallises with difficulty in colourless warty

masses, resolved into liquid itaconic acid,  $C_5H_6O_4$ , by heating to  $160^\circ C$ . Aconitic acid is soluble in water, alcohol, and ether; the last solvent may be employed to separate it from citric acid. Aconitic acid crystallises more readily than maleic, and is more soluble in water than fumaric acid. Its aqueous solution has a decided acid reaction, and a sour taste.

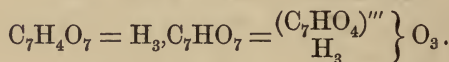
Many of the aconitates are insoluble. Mercurous aconitate is precipitated on adding mercurous nitrate to a solution of free aconitic acid. Aconitate of calcium requires 100 parts of cold water for solution, and is much more soluble in boiling water. If the solution be treated with lead acetate, insoluble aconitate of lead is precipitated, which, if decomposed by sulphuretted hydrogen, yields free aconitic acid.

When perfectly free from citric acid, aconitic acid does not prevent the precipitation of ferric solutions by ammonia. Citric acid may be detected in aconitic acid by converting the acid into a barium salt, and examining the crystals microscopically; barium citrate assumes very characteristic forms.

## MECONIC ACID.

*French*—Acide Meconique.

*German*—Mohnsäure; Opiumsäure.



This acid exists ready formed in opium, from which it is obtained by precipitating the neutralised aqueous solution of the drug with calcium chloride or lead acetate; this produces an insoluble meconate, which is subsequently decomposed by a mineral acid. Meconic acid crystallises in micaceous scales or small rhombic prisms, containing 3 Aq. On being heated to  $100^\circ C$ , meconic acid loses its water of crystallisation, and leaves a white effloresced mass.

On heating to  $120^\circ C$ , meconic acid splits up into carbon dioxide, and comenic acid,  $H_2.C_6H_2O_5$ , which at a higher

temperature again loses carbon dioxide, and forms pyro-comenic acid,  $\text{H}_5\text{C}_5\text{H}_3\text{O}_3$ . Comenic acid is but sparingly soluble in hot, and is almost insoluble in cold water. In absolute alcohol it is quite insoluble. Meconic acid dissolves in 115 parts of cold, or a smaller quantity of boiling water; its solubility is diminished by addition of hydrochloric acid, which therefore causes a precipitate in strong solutions. When the solution of meconic acid is boiled for some time, especially if hydrochloric acid be present, comenic acid is formed, and crystallises out as the liquid cools. The aqueous solution of meconic acid has a sour astringent taste, and strongly acid reaction.

Meconic acid is freely soluble in alcohol (distinction from comenic acid), less readily so in ether.

Nitric acid readily acts on meconic acid, much oxalic acid being formed.

Meconic acid derives its chief analytical interest from the fact that it is peculiar to opium and its preparations, and hence its positive detection is a decided proof of the presence of a preparation of opium. The best mode of extracting meconic acid from opium is described on the next page.

The most characteristic reaction of meconic acid is the formation of a deep purplish-red coloration on adding ferric chloride to the solution of meconic acid or a meconate. \*The colour differs from that of the acetate of iron, in not being readily destroyed by boiling, or by adding cold dilute hydrochloric acid, and from the ferric thiocyanate by being unaffected on addition of mercuric chloride (see page 60). If any doubt exist as to the presence of an acetate, it is desirable to precipitate the solution with neutral acetate of lead, wash the precipitated lead meconate thoroughly, suspend it in water, and decompose it with sulphuretted hydrogen. After evaporating the filtered liquid at a gentle heat to drive off the excess of sulphuretted hydrogen, the test with ferric chloride may be safely applied.



Comenic Acid reacts like meconic acid with ferric chloride.

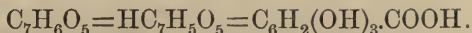
Meconic acid may be determined by converting it into a lead salt, or colorimetrically by ferric chloride, by comparing the depth of tint produced by the sample with that obtained by treatment with a known quantity of opium. Very fair approximate estimations of meconic acid, and less accurately of opium, may be made in this way, even when the quantity of material at disposal is very insignificant.

**Meconates**,  $\text{MH}_2\text{C}_7\text{HO}_7$ ;  $\text{M}_2\text{HC}_7\text{HO}_7$ ; and  $\text{M}_3\text{C}_7\text{HO}_7$ .—Meconic acid forms three classes of salts, the more basic of which are usually insoluble in water, with the exception of the meconates of the alkali-metals. The meconates having two atoms of basic hydrogen replaced by metals are neutral to test paper. The meconates are nearly all insoluble in alcohol, and are but slightly affected by acetic acid.

**ACID CALCIUM MECONATE**,  $\text{CaH}_4(\text{C}_7\text{HO}_7)_2$ , is precipitated as a sparingly soluble salt, on adding calcium chloride to a solution of meconic acid or a soluble meconate. In presence of free ammonia less soluble yellow dicalcic meconate,  $\text{Ca}_2\text{H}_2(\text{C}_7\text{HO}_7)_2$ , is precipitated. On treating either of these salts with hot dilute hydrochloric acid, meconic acid crystallises out on cooling.

**IRON MECONATES.** Ferrous meconate is a very soluble colourless salt, which turns red on exposure to air. Ferric meconate exists in the purple-red liquid produced on adding a ferric salt to a soluble meconate.

**LEAD MECONATE**,  $\text{Pb}_3(\text{C}_7\text{HO}_7)_2 \cdot \text{H}_2\text{O}$ , is produced by precipitating meconic acid or a meconate (or an aqueous solution of opium) with neutral acetate of lead. It is quite insoluble in cold and boiling water, and is not affected by acetic acid. When suspended in water and decomposed by a stream of sulphuretted hydrogen, it yields meconic acid, which can be obtained in crystals by adding hydrochloric acid to the filtered and concentrated solution. This is the most satisfactory method of extracting meconic acid from opium.

**GALLIC ACID.****Dioxy-Salicylic Acid.**

Gallic acid exists ready formed in many plants, and is also obtained by the metamorphosis of gallo-tannic acid, which, in the presence of air and of a nitrogenised body called pectase, splits up with formation of gallic acid and glucose. It also results from the action of boiling dilute acids on the tannin of galls.

Gallic acid forms white or light brown crystalline needles, containing 1 atom of water ( $9\frac{1}{2}$  per cent.), which it loses at  $100^\circ\text{C}$ . It is soluble in 100 parts of cold, or 3 of boiling water. The solution has an acid and astringent taste, and decomposes on keeping. Gallic acid is also soluble in rectified spirit and in glycerin, and is slightly soluble in ether.

When heated to a temperature of about  $210^\circ\text{C}$ ., gallic acid is decomposed with production of carbon dioxide and the formation of a crystalline sublimate of pyrogallic acid,  $\text{C}_6\text{H}_6\text{O}_3$  (see page 281). If the heat be raised suddenly to  $250^\circ\text{C}$ . the results are different; in addition to carbon dioxide, water is given off, and in the retort there is found a considerable proportion of dark lustrous material consisting chiefly of meta-gallic acid, ( $\text{C}_6\text{H}_6\text{O}_3 = \text{C}_6\text{H}_4\text{O}_2 + \text{H}_2\text{O}$ ).

When an infusion of gall-nuts is exposed to the air for some time, in addition to gallic acid, a substance called ellagic acid,  $\text{C}_{14}\text{H}_8\text{O}_9$ , is deposited. This substance is nearly insoluble in water, alcohol, and ether, and is known to tanners under the name of "bloom."

Aqueous solution of gallic acid gives the following reactions:—

1. Solution of ferric chloride gives a deep-blue coloration, which is destroyed by boiling.
2. Solution of ferrous sulphate, if free from ferric salt, produces a white precipitate in strong solutions, but no change in

dilute liquids. The solution or precipitate rapidly acquires a bluish-black colour by oxidation.

3. On addition of excess of alkali the liquid turns yellow and ultimately brown and black on exposure to the air, from formation of tanno-melanic acid. The reaction is accelerated by boiling. On neutralising the black liquid with acetic acid and adding lead acetate, a black precipitate is thrown down.

4. Solution of tartar-emetic ( $K(SbO)\bar{T}$ ), precipitates white gallate of antimony, even from very dilute solutions. The reaction is prevented by chloride of ammonium.

5. Gallic acid does not reduce Fehling's solution, but reduces gold and silver solutions (rapidly when hot), and decolorises permanganate.

6. No precipitate (distinction from tannic acids) is produced by solutions of gelatin, albumin, or starch, but a mixture of gum-arabic and gelatin is precipitated.

7. Lime water in excess produces a white precipitate, changing through blue and violet to purple.

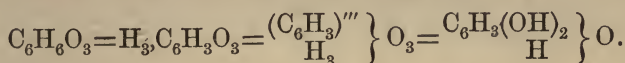
COMMERCIAL GALLIC ACID is liable to contain inorganic matter, detected by ignition in the air; and tannic acid, which precipitates a solution of gelatin.

GALLIC ACID MAY BE DETERMINED, in absence of other reducing agents, by titration in an acid solution with potassium permanganate. If the process be modified by first precipitating the solution with gelatin, tannin does not interfere. For details, see page 292.

Another method depends on the insolubility of cupric gallate in water, and its solubility in ammoniacal liquids. The solution is precipitated by excess of cupric acetate, the precipitate washed and digested with a cold solution of ammonium carbonate. The solution, filtered from any insoluble tannate of copper, is evaporated to dryness, the residue moistened with nitric acid, ignited, and the resultant cupric oxide weighed. Its weight, multiplied by 0.9, gives the weight

of gallic acid, making due allowance for a little tannate which dissolves in the ammoniacal liquid. This method is applicable to the separation of gallic acid from gallo-tannic and querci-tannic acids, but the copper salts of many varieties of tannin are soluble in ammonium carbonate.

**Pyrogallic Acid.** Pyrogallin; Pyrogallol; Dioxyphenol.



This substance is prepared by heating gallic acid or an aqueous extract of gall-nuts to a temperature of about  $210^\circ \text{C}$ . when it sublimes in prismatic plates, which fuse at  $131^\circ \text{C}$ .

Pyrogallic acid has an acid and very bitter taste. It is soluble in less than 3 parts of cold water, and is still more soluble in hot. It is also freely soluble in alcohol and ether, but is not dissolved by absolute chloroform.

Its acid properties are very feebly marked.

Pyrogallic acid is permanent in dry air free from ammonia, but in moist or ammoniacal air it gradually darkens, and in aqueous solution it turns brown or black, especially when the liquid is heated. In presence of ammonia or fixed alkalis, it absorbs oxygen from the air with the greatest avidity, the liquid becoming first purplish and then dark brown; the colour is destroyed by oxalic acid. Fehling's solution and solutions of gold and silver are rapidly reduced, and permanganate is decolorised in acid solutions with evolution of  $\text{CO}_2$ . With lime water a purplish-red colour, turning brown, is produced, but no precipitate is formed. With ferrous sulphate a blue solution is formed, and with ferric chloride a red coloration, turning brown when heated. Pyrogallic acid does not precipitate a solution of gelatin.

Pyrogallic acid may be determined by titration in acid solution with standard permanganate (see page 292). In presence of gallic acid it might probably be determined by Fehling's solution.



**TANNINS or TANNIC ACIDS.**

Under the name of tannin or tannic acid are known, and to a great extent confused, a considerable number of vegetable acids having great analogy to each other, but possessing distinct individuality.

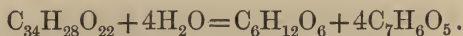
The different varieties of tannin or tannic acid agree in the following general properties:—

TANNIC ACIDS are amorphous or sub-crystalline solids, not fusible or volatile, freely soluble in water and alcohol, but generally little soluble in dilute sulphuric acid. Their aqueous solutions give blue or green colours or precipitates with ferric salts, and precipitate solutions of gelatin and albumin. The combinations of tannins with gelatin are remarkably stable. Hence, tannic acids can be removed from their aqueous solutions by the introduction of skin or rasped hide. They are also removed from solution by digestion with cupric or zinc oxide, and are all precipitated by acetate of copper or lead. A delicate reaction for tannins (first noticed by the author) is the deep red colour produced on treating a solution with potassium ferricyanide mixed with ammonia. Tannic acids give insoluble precipitates with many organic bases. The rosaniline and cinchonine precipitates are among the least soluble.

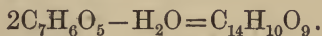
The most characteristic property of the active astringent principles (tannins) contained in plants used for tanning is the formation, by combination with gelatin and albumin, of the insoluble compounds which constitute leather.

**Constitution of Natural Tannins.**—The natural tannins may be arranged in two great classes, namely, those like catechu-tannin, which are fairly stable, and those like the tannin of galls, which are liable to decomposition with formation of products useless for tanning purposes. It has been shown by H. Schiff that the ordinary tannin of galls (gallo-tannic acid) is really a glucoside, and that under the influence of dilute acids, or of a peculiar nitrogenous

ferment called pectase, it readily splits up into glucose and gallic acid,



From Schiff's researches it appears that the natural tannin of galls is a glucoside of digallic acid. He effected the synthesis of digallic from gallic acid, and obtained a product which gave a blue-black precipitate with ferric salts, yielded pyrogallic acid on dry distillation, and was converted into gallic acid on boiling with dilute acid, without the formation of a trace of glucose. He therefore suggests the abandonment of the term tannic acid, and proposes the name digallic acid for the above compound, restricting the term tannin to the natural glucosides. Digallic acid is the first anhydride of gallic acid; thus,



Or, regarding gallic acid as an alcohol, digallic acid is the ether.

Commercial Tannin from Galls is an indefinite mixture of digallic acid and the glucoside. That this view is correct is evident from the fact, that it yields from 0 to 22 per cent. of glucose when acted on by dilute acids. The glucoside,  $\text{C}_{34}\text{H}_{28}\text{O}_{22}$ , would yield 23 per cent. This conclusion is fully confirmed by collateral evidence.

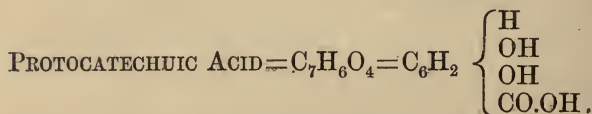
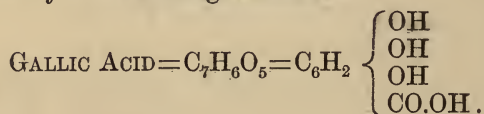
It has been suggested by Hlasiewetz that the natural tannins are not true glucosides, but bodies which would be more correctly regarded as gummides or dextrides, and hence that the formation of glucose by the action of dilute acids is due merely to a secondary action on the gum or dextrin. Other glucosides are certainly more distinctly crystalline and more readily split up by acids than the tannins.

Stenhouse found that certain varieties of tannin yield pyrogallic acid when subjected to dry distillation, while from others it is not obtainable. The tannin of sumach (and probably of myrobolans and many other materials) has been proved iden-

tical with that of galls, and it is probable that only this variety of tannin (which is often called gallo-tannic acid) yields pyrogallie acid when heated, other tannins being decomposed with formation of different products. According to Hlasiewetz, the following are the results of acting on various kinds of tannin by dilute sulphuric acid, and by fused caustic potash:—

	Boiled with Dilute <i>Sulphuric Acid.</i>	Fused with <i>Caustic Potash.</i>
Pomegranate tannin yields	Glucose and ellagic acid	Gallic (?) acid.
Gall           "       "	"       gallic   "	{ Pyrogallie and car- bonic acids.
Coffee       "       "	"       caffie   "	{ Protocatechuic and acetic acids.
Cinchona ( <i>a</i> )   "       "	"       china   red	"       "
Cinchona ( <i>b</i> )   "       "	"       chinova   "	"       "
Fern       "       "	"       filix     "	"       "
Ratanhia   "       "	"       ratanhia   "	{ Protocatechuic acid and phloroglucin.
Chestnut   "       "	(?)   chestnut   "	"       "
Catechu   "       "	"       catechin   "	"       "

The relationship between gallic and protocatechuic acids is well shown by the following formulæ:—



PHLOROGLUCIN has the formula  $\text{C}_6\text{H}_6\text{O}_3 = \text{C}_6\text{H}_3(\text{OH})_3$ .

In instances in which pyrogallie acid is formed, it may be assumed to be produced by the action of heat on gallic or digallic acid. Pyrogallie acid is isomeric with phloroglucin.

Some varieties of tannin, as those from galls and oak-bark, give a bluish-black coloration with ferric salts, while others give a decided green tint. It has been suggested by Stenhouse that the former class are glucosides, readily split up

under the influence of pectase with formation of gallic acid. There appears, however, to be no very sharp distinction, varieties of tannin which yield no gallic acid being often readily changed with formation of useless insoluble red colouring matters. The coloration given with ferric salts is often much modified by foreign matters, and but little reliance can be placed on the test as a means of distinguishing one class of tannins from another.

In consequence of the natural tannins being merely analogous bodies, and not strictly identical with each other, their saturation equivalents are dissimilar. Hence when a process applicable to the determination of gallo-tannic acid is employed for the assay of other tanning materials, the results are not true expressions of the amounts of tannin present, but merely of their equivalent amounts in terms of gallo-tannic acid.

The following table gives the names, formulæ, sources, and leading properties of some of the natural tannins. The formulæ are in many cases very doubtful.

Name.	Formula.	Source.	Reaction with Ferric Salts.	Remarks.
Gallo-tannic acid } (Digallic acid)	$C_{14}H_{10}O_9$	Gall-nuts.	Blue-black.	} See pages 283 and 286.
Gallo-tannic acid } (Glucoside of)	$C_{34}H_{28}O_{22}$	Gall-nuts.	Blue-black.	
Alder tannin . .	$C_{27}H_{28}O_{11}$	{ Alder wood. Alder bark.	Dirty green. Blue-black.	
Sumach tannin . .	$C_{16}H_{14}O_{10}$	Sumach leaves.	Greenish.	According to Lowe, identical with gall-tannin.
Sali-tannic acid . .	...	Willow bark.	Deep black.	Formula very doubtful. Does not precipitate gelatin. Precipitates cinchonine. The tincture gives green with tincture of ferric chloride. The tincture gives blue-black with tincture of ferric chloride.
Querci-tannic acid .	$C_{14}H_{16}O_8$	Oak bark, &c.	Blue-black.	
Ulmò-tannic acid . .	...	Elm bark.	Dirty green.	
Lupulo-tannic acid	$C_{50}H_{40}O_{25}$	Hops.	...	
Caffe-tannic acid .	...	Coffee.	Green.	Crystallisable. Gives phenol on heating. Does not precipitate tartar-emetie.
Bohea-tannic acid .	$C_7H_{10}O_6$	Black tea.	Brown.	
Tea tannin . . .	...	Green tea.	...	
Quino-tannic acid .	...	Cinchona bark.	Green.	
Mori-tannic acid .	$C_{13}H_{10}O_6$	Fustic.	Greenish.	
Mimo-tannic acid .	$C_{15}H_{14}O_{11}$	Catechu.	Greenish.	



**Commercial Gallo-tannic Acid** often contains more or less chlorophyll, volatile oil, gallic and ellagic acids. Specimens containing chlorophyll when shaken with an equal weight of water and the same volume of ether, colour the ethereal layer more or less greenish. Gallic acid may be detected by leaving the aqueous solution of the sample in contact with a piece of untanned skin, and agitating the liquid from time to time. If the tannin be pure it is entirely absorbed, and the liquid becomes insipid, and no longer gives a coloration with ferric chloride; the contrary being the case if gallic acid be present.

For the constitution of commercial gallo-tannic acid, see p. 283.

The following reactions are distinctive between solutions of gallic, pyrogallic, and gallo-tannic acids :—

	Gallic Acid.	Pyrogallic Acid.	Gallo-tannic Acid.
1. With solution of gelatin.	No change (except in the presence of gum).	No change.	White or brownish precipitate.
2. Heated with Fehling's solution.	No change.	Reduction, and precipitation of $\text{Cu}_2\text{O}$ .	Reduction, and precipitation of $\text{Cu}_2\text{O}$ .
3. With ferrous sulphate free from ferric salt.	White, concentrated; no change, dilute.	Blue solution.	White, concentrated; no change, dilute.
4. With ferric chloride.	Deep-blue colour destroyed by boiling.	Red colour, turning brown when heated.	Blue-black precipitate; colour destroyed by boiling.
5. With excess of lime-water.	White precipitate becoming purple or deep-brown very rapidly.	Immediate purple colour, changing to brown in the air.	White precipitate, slowly darkening.

Watson says they may be distinguished as follows :—

	Gallic Acid.	Pyrogallic Acid.	Gallo-tannic Acid.
To the solution of about $\frac{1}{2}$ grain of the sample in a little water add ammonia.	Pink colour, rapidly changing to deep-orange solution.	Lemon-coloured solution.	Same as with gallic acid.
To a portion of the ammoniacal liquid add nitric acid.	Red colour.	Red colour.	Purple precipitate, insoluble in excess of $\text{HNO}_3$ .
To a portion of the ammoniacal solution add hydrochloric acid.	Red colour.	Pink colour, changing to black.	Pink precipitate, soluble in excess.

## Tannin-yielding Materials.

The following table gives the common names of the principal tannin-yielding substances used in commerce, together with the botanical names of the plants producing them, the parts of the plant used, and the usual percentage of tannin contained in good specimens of each material:—

Common Name of Material.	Botanical Name of Plant.	Part of Plant Used.	Average per cent. of Tannin.
Oak bark . . .	<i>Quercus pedunculata</i> and <i>Q. robur</i> .	Bark.	8-13
Cork bark . . .	<i>Quercus suber</i> .	Inner bark.	10-14
Valonia . . .	<i>Quercus ægilops</i> .	Acorn-cups.	25-35
Chestnut oak } extract . . }	<i>Quercus</i> (an American species).	Extract from bark.	20-25
Hemlock bark .	<i>Abies Canadensis</i> .	Bark.	10-12
" extract	<i>Abies Canadensis</i> .	Extract from bark.	18-25
Churco bark . .	<i>Oxalis gigantea</i> (Chill). ?	Bark.	26
Monesia bark .	<i>Chrysophyllum glycyphloeum</i> .	Bark.	32
Mangrove bark .	<i>Rhizophora mangla</i> .	Bark.	22-33
Alder bark . .	<i>Alnus glutinosa</i> .	Bark.	16
Larch bark . .	<i>Abies larix</i> .	Bark.	6-8
Mimosa (Wattle)	<i>Acacia dealbata</i> and <i>A. molissima</i> .	Bark.	24-30
Catechu (Cutch)	<i>Acacia</i> and <i>Areca catechu</i> .	Extract from wood.	45-55
Gambier . . .	<i>Uncaria gambir</i> .	{ Extract from leaves and small branches. }	36-40
Terra japonica .	<i>Butea frondosa</i> .	Do. do.	42-50
Sumach . . .	<i>Rhus coriaria</i> and <i>R. cotinus</i> .	Leaves.	14-18
Chestnut wood .	<i>Castanea vera</i> .	Wood.	8-10
" extract	<i>Castanea vera</i> .	Extract from wood.	14-20
Quebracho wood	<i>Aspidospermum quebracho</i> .	Wood.	14-16
Marsh Rosemary	<i>Statice coriaria</i> .	Root.	20-24
Ratanhy . . .	<i>Krameria triandria</i> .	Root.	38-42
Myrabolans . .	<i>Terminalia cherbula</i> and <i>T. belerica</i> .	Fruit.	20-40
Divi-divi . . .	<i>Cæsalpina coriaria</i> .	Pod.	50-56
Kino . . .	{ <i>Pterocarpus marsupium</i> , and <i>Dre-</i> <i>panocarpus senegalensis</i> . }	Extract from fruit.	75
Gall-nuts . . .	<i>Quercus infectoria</i> , &c.	Galls.	65-77
Tamarisk galls .	<i>Tamarix Indica</i> , and <i>T. Africana</i>	Galls.	50-54
Rove . . .	? (Greece and Asia Minor).	Galls.	24-34

The above table sufficiently indicates the nature of the principal tanning materials, but a few of them require a somewhat more detailed description.

CATECHU or CUTCH, is the dried extract from the wood of the *Acacia* and *Areca catechu*. It is very similar in nature to *Gambier* and *Terra japonica*. Cutch, however, produces a hard red leather, like *Mimosa*, and generally occurs in more or less brittle, splintery masses. Gambier occurs in light, porous, brown cubes, more or less adherent, or in blocks measuring 2 feet × 1 foot × 9 inches.

In addition to a large proportion of a variety of tannin (mimotannic acid,  $C_{15}H_{14}O_{11}$ ), catechu contains 30 or 40 per cent. of catechin, which forms a white tasteless powder or silky needles, melting at  $217^{\circ}$  C. It does not precipitate tartar-emetic, gelatin, or alkaloids. It gives a deep purple liquid with sulphuric acid. Catechin is deposited on cooling a boiling aqueous solution of catechu.

Catechu is not unfrequently adulterated, starch, sand, clay, and blood being among the materials employed for the purpose. Catechu should not contain more than 5 per cent. of ash. Starch may be detected by treating the sample with alcohol, boiling the insoluble residue with water, and testing the cold liquid with iodine, which gives the well-known blue colour in presence of starchy matters. The presence of ordinary tannin-matters is indicated by the modified colour which the sample gives with ferric salts. Pure catechu gives a decided green. Blood may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and most offensive vapours will be produced. Aqueous solution of catechu should give with alcohol or gelatin an abundant precipitate; with salts of tin and lead, yellow precipitates of various tints; and a brown precipitate with bichromate of potassium. It should take a decided brown hue with alkalies, and give a greenish colour with ferric chloride. Good catechu yields at least half of its weight to ether.

KINO generally occurs in irregular black fragments, but is also met with in round cakes. Thin slices are often transparent and of a reddish colour; the powder is red. Kino should be completely soluble in hot water, forming a red liquid precipitated on addition of alcohol. Kino is sometimes adulterated, the usual sophistications being dragon's blood, pitch, catechu, and ratanhy extract. The last substance may be distinguished from kino by touching a fragment of the sample with the tongue; kino remains reddish-brown, but ratanhy extract

takes a fine bronze tint, which lasts as long as the surface of the fragment is wet. The ash of kino should not exceed 3 or 4 per cent.

GALL-NUTS are the most valuable and important of all tannin matters.\* They are the produce of the female of an insect called *cynips* (gall-wasp), which pierces the buds on the young branches of the *Quercus infectoria* and other species of oak. The eggs therein deposited soon hatch, while the bud loses its natural growth and swells out to the size of a hazelnut. When perfect, the insect punctures a hole and escapes. Good gall-nuts should not be so pierced; they should be heavy, and of a fresh green colour ("green galls"). If the insect has escaped, they are yellow and inferior ("white galls").

Worm-eaten galls are sometimes doctored by filling the holes with wax. The fraud may be detected by immersing the galls in boiling water, which melts the wax and renders the holes visible. Exhausted galls are occasionally coloured by washing them with a solution of ferrous sulphate, which is readily detected by its chemical reactions.

Chinese gall-nuts are a production of the *Rhus semialata*. They are very light and hollow, and distorted by numerous protuberances, and are completely covered by a thick velvety grey down. Chinese galls are much used for the preparation of tannin, of which they contain about 70 per cent. English galls from the common oak are much inferior to the foreign varieties. They are smooth, brown, and slightly speckled with pale-brown excrescences.

**Determination of Tannin.**†—A great variety of methods

\* A sample of gall-nuts analysed by Guibourt contained,—tannic acid, 65.0; gallic acid, 2.0; ellagic and luteo-gallic acid, 2.0; chlorophyll and volatile oil, 0.7; brown extractive matter, 2.5; gum, 2.5; starch, 2.0; woody fibre, 10.5; sugar, albumin, and ash, 1.3; water, 11.5 per cent.

† The methods of assaying tannin-yielding materials have been ably examined recently by Mr H. R. Procter, and it is chiefly from his observations that the abstract in the text is abridged. I am also indebted to Mr Procter for a very valuable revision of the entire article on tanning materials.



have been described for determining tannin and assaying tannin-yielding materials. In a great many instances the authors have ignored the fact that gallic acid, while reacting in many respects like tannin, does not form insoluble compounds with gelatin and albumin, and hence is valueless for the purpose of tanning.

1. An apparently plausible method of assaying tanning materials is to force the infusion through a piece of raw hide, noting the decrease in the specific gravity of the solution. In practice, however, it is very difficult to secure complete absorption of the tannin, while in other cases foreign substances are also taken up by the membrane. In fact, the errors are so great that the results have little practical value, the same sample giving from 18 to 28 per cent. of tannin in nine experiments, in every one of which complete absorption of the tannin was proved to have occurred. As oak-tannin is worth about 10s. per unit (per ton of bark), these differences are quite intolerable. The older method, in which a known quantity of rasped hide is immersed in the solution, is still more inaccurate. It is also very doubtful whether the same or equivalent weights of the different varieties of tannin affect the density of a solution to the same extent. Below 5 per cent., an aqueous solution of gallo-tannic acid increases in density by  $\cdot 0004$  for every  $\cdot 1$  per cent. of tannic acid present. Hence, a 5 per cent. solution has a density of 1.0200. Above 5 per cent., the increase is slightly more rapid, a 10 per cent. solution having a density of 1.0406, and 15 per cent. of 1.0614, while a 20 per cent. solution has a density of 1.0824.

2. Another much used method is to precipitate the solution with a standard solution of gelatin and alum. Under favourable circumstances it is possible to get rough results by this method, but the solution of gelatin undergoes extremely rapid change, and the end of the reaction is very difficult to observe. In addition to these objections, the results appear liable to some undiscovered source of error.

3. The old method of precipitating the liquid with gelatin, drying and weighing the precipitate, and reckoning 40 per cent. of its weight as tannin, is both tedious and inaccurate; when sufficient alum is added to cause the precipitate to coagulate, and it is then washed with boiling water by decantation, fairly good results are said to be obtainable.

4. Another method has been based on the fact that while tannin, gallic acid, and colouring matter are all precipitated by cupric acetate, the two latter precipitates are redissolved by ammonium carbonate. The cupric precipitate from tannins giving a blue-black reaction with ferric salts is insoluble in the ammoniacal liquid, but those tannins giving a green colour with iron yield precipitates with acetate of copper which are very sensibly soluble in ammoniacal liquids. The precipitate must be rapidly and carefully washed and ignited. The residue should be moistened with nitric acid and re-ignited. The tannin may be taken at twice the weight of cupric oxide found. For determining tannin in wine this method is very serviceable.

5. Another method, partly originating with the author, is based on the precipitation of the tannin from a hot solution by a standard solution of lead acetate, the end of the reaction being ascertained by filtering the liquid, and testing it for tannin by ammoniacal ferricyanide. The process was originally described as a method of assaying tea,\* and was selected partly because the indications included any gallic acid which might be present or be formed. Hence, it is not fitted for the assay of tannin materials without some modification. By employing the method on the original infusion of the sample, and again after treatment with hide raspings or Nelson's gelatin swollen in cold water, very fair results are obtainable, but the repeated filtrations necessary to observe the end-reaction render the process tedious.

\* *Chem. News*, xxix. pages 169 and 189.

6. The above methods of determining tannin are only described in outline, and with a view of pointing out their imperfections, for they are in every respect inferior to a process invented by Estcourt and improved by Löwenthal. This is based on the fact that tannin is oxidised in acid solutions by permanganate, though the slowness of the oxidation and the want of definition of the end-reaction render the method unsuitable without modification. By addition of a considerable quantity of indigo, the oxidation of the tannin is controlled, and the end-reaction is rendered perfectly definite. The details of the process are as follow:—

10 grammes of a sample of sumach or valonia, or 20 grammes of finely-ground bark,\* are exhausted by repeated boilings with water, and the infusion when cold made up to 1 litre.

10 c.c. of this solution are diluted to 800 or 1000 c.c. by distilled or good drinking water, and 25 c.c. of a solution containing about 6 grammes of "pure precipitated indigo," and 50 c.c. per litre of concentrated sulphuric acid are added. A  $\frac{1}{20}$ th normal solution of permanganate of potassium (or better, a solution of 1 gramme per litre) is then added drop by drop from a burette, with constant stirring, until the blue colour of the indigo changes to a clear yellow. The process is next repeated without the addition of the infusion of tannin. The difference shows the volume of permanganate decolorised by 10 c.c. of the solution of the sample.

100 c.c. of the tannin infusion are next mixed with 50 c.c. of a liquid made by dissolving 25 grammes of good transparent glue in hot water, diluting to 1 litre, and saturating the solution with good common salt. To the whole is next added 100 c.c. of a saturated solution of common salt, containing 25 c.c. of strong sulphuric acid to the litre. The mixture is left standing for several hours and is then filtered from the

\* H. R. Procter recommends the use of half the above quantities, and 20 c.c. of indigo solution, instead of 25 c.c. Prudhomme uses aniline green in place of indigo, but the substitution is not advantageous.

precipitated tannin, the gallic acid and impurities remaining in solution. 50 c.c. of this filtrate (equal to 25 c.c. of the original solution), are then mixed with 25 c.c. of the indigo solution, and titrated with permanganate as before. The amount used, less that previously found to be required to oxidise 25 c.c. of the indigo solution, represents the gallic acid and impurities in 25 c.c. of the infusion, and this multiplied by 4 and deducted from the permanganate required by 10 c.c. of the original infusion (less that used by the indigo alone) gives the permanganate corresponding to the real leather-forming tannin in 10 c.c. of the infusion. It is desirable to repeat all the titrations. The results should not vary by more than 0.1 c.c. of permanganate, or  $2\frac{1}{2}$  per cent. of the total quantity. The above process has been thoroughly examined by Kathreiner, who fully confirms its accuracy, but recommends the observance of the following precautions. The amount of permanganate decolorised in any titration by the indigo alone should be at least two-thirds of the total quantity used; otherwise it may all be oxidised before the tannin is completely acted on. The tannin solutions may be kept for two or three days if protected by the addition of 0.5 c.c. of glacial acetic acid. The titration should be conducted in a white porcelain dish, and the permanganate added very slowly, not less than five or six minutes being taken for the process. A slight error is introduced by the oxidisable matters contained in the "finest Cologne glue," used for preparing the gelatin solution. As different samples of glue may have a different influence in this respect, it is desirable to make a blank analysis with gelatin and indigo solutions alone, and to deduct the volume of permanganate thus used from the total quantity required by the "not tannin" bodies.

Other operators have recommended the employment, instead of gelatin, of an ammoniacal solution of cupric or zinc acetate for precipitating the tannin matters, but some tannins are not perfectly precipitated by ammoniacal cupric solutions, and



Kathreiner found the zinc method to give very discordant results. For the determination of the tannin in wines, the zinc process appears well suited. (See below.)

Neubauer estimates each c.c. of  $\frac{1}{20}$ th normal permanganate as equivalent to 0.002078 of gallo-tannic acid, or 0.003118 of oak-bark tannin. This first factor is applicable to sumach, galls, and myrabolans, and the second probably to oak-bark, valonia, chestnut-extract, &c. Gallic acid consumes a larger volume of permanganate than the tannin from which it is derived. Hence, as commercial tannin is often largely contaminated with gallic acid, it not unfrequently assays over 100 per cent. of tannin.

It cannot be too clearly understood that Löwenthal's and all other processes for the assay of tannins are merely comparative, and give results worthy of acceptance only when they are used for comparing the qualities of samples of material of the same character. Thus, bark may be compared with bark, valonia with valonia, and cutch with cutch, but it will not do to make *cross comparisons* at random, though the same process should give absolute results of at least approximate accuracy when applied to different materials containing the same variety of tannin.

7. FOR THE DETERMINATION OF THE TANNIN IN WINES, A. Carpené\* recommends the use of ammoniacal acetate of zinc containing a large excess of ammonia, which has the property of forming with wine-tannin a tannate of zinc quite insoluble in water, in ammonia, and in excess of the reagent itself, while it gives no precipitate with alcohol, malic or tartaric acid, tartrates, glycerin, gelatin, albumin, or the iron salts of organic acids. With gallic and succinic acids, glucose, and salts of aluminium, it forms precipitates soluble in excess of the reagent and in ammonia.

On treating the sample of wine with an excess of zinc acetate, a precipitate is formed consisting of zinc tannate mixed

\* *Gazetta Chimica Italiana*, v. 120; *Journ. Chem. Soc.* 1875, p. 1054.

with a small quantity of colouring matter. The wine is heated nearly to boiling to agglomerate the precipitate, which, after cooling, is filtered off and washed with a little boiling water, to remove adherent colouring matter. The precipitate is dissolved in dilute sulphuric acid, and the solution so obtained titrated with standard permanganate and indigo, as described on page 292. Each c.c. of a  $\frac{1}{1000}$  normal solution of permanganate is said to oxidise  $\cdot 0076^*$  grammes of wine-tannin. The results by this method are stated to be very accurate.

**Writing Inks.**—Ordinary writing ink was formerly always made from a decoction of galls, to which green vitriol was added. Of late the composition of writing inks has become far less constant, aniline and other dyes being frequently employed, and other metallic salts substituted for the ferrous sulphate formerly invariably used.

Writing inks are either coloured liquids, or liquids containing a finely divided precipitate in suspension. The best black ink is a tanno-gallate of iron, obtained by adding an infusion of nut-galls to a solution of ferrous sulphate (copperas). The galls contain gallic and gallo-tannic acids; on coming in contact with ferrous salts in concentrated solutions, these produce white precipitates which turn black on exposure to air. With ferric salts, blue-black precipitates are at once produced. A small quantity of gum is added to retain the precipitate in suspension. To ink intended for copying by pressure, a small addition of sugar or glycerin is also made.

Logwood is a frequent constituent of ink. It gives the original ink a darker hue, and itself contains tannin.

Sulphate of copper is sometimes added to ink, with questionable advantage.

A very cheap and perfect ink is obtained by dissolving 24 parts of extract of logwood in 1000 of water, and adding 2

\* There seems to be some mistake here. Either a  $\frac{1}{10}$  normal solution of permanganate is intended to be used, or 100 c.c. of the weaker solution would probably be required for the oxidation of  $\cdot 0076$  grammes of tannin.

parts of neutral chromate of potassium. This ink is a deep black liquid, which, unlike that made with tanno-gallate of iron, contains no deposit.

Indelible ink usually owes its property to an admixture of finely divided carbon, to which indigo is sometimes added. It is kept in suspension by gluten, an alkaline solution of shellac, or other similar means.

The following table shows the general composition of black writing-inks, and sufficiently indicates the substances to be sought for by the analyst:—

	Superior Ink.	Inferior Ink.	Ink containing Vinegar.	Logwood Ink.	Copying Ink.	Copper Ink.	Runge's Chrome Ink.	Copying Ink.	Ink Powder.	Stephen's Blue-black Ink.
Galls . .	225	62	174	50	60	42	...	..	12	15
Logwood . .	...	...	...	100	21	20	140	4	...	...
Potassium Chromate	...	...	...	...	...	...	1	...	...	...
Ferrous sulphate	75	31	87	16	20	21	...	3	4	5
Cupric sulphate	...	...	...	...	...	5	...	...	...	4 iron filings.
Alum . .	...	...	...	...	...	...	...	2	...	...
Gum . .	25	31	43	47	20	16	...	3	2	...
Sugar . .	...	...	...	28	1000(?)	...	...	5	1	...
Vinegar . .	...	...	135	...	...	...	...	60	...	...
Water . .	1000	1000	1000	...	1000	1000	1000	70	...	200
										$\frac{1}{2}$ indigo in 3 of sulphuric acid.

In analysing ink, the total solid residue should be determined by evaporating 50 c.c. to dryness on the water-bath. The residue thus obtained is first weighed and next ignited, the odour produced on heating being carefully noted; sugar or shellac may thus be detected. The weight of the ignited residue is then taken, after which it is fused in platinum with potassium chlorate and alkaline carbonate. The mass is extracted with hot water, filtered, and the solution acidulated with acetic acid. In presence of a chromate, the liquid will have a yellow colour, and will give a chrome-yellow

precipitate on adding a single drop of acetate of lead. This process may be applied quantitatively, if the lead solution be added in slight excess, and the precipitated  $\text{PbCrO}_4$  be collected and weighed. The residue left on treating the fused mass with water should be boiled with hydrochloric acid, the liquid filtered and examined for iron, copper, aluminium, &c., in the usual way. By precipitating the solution with a large excess of ammonia, the iron and aluminium may be roughly separated from the copper, which remains in solution and communicates a blue colour to the liquid.

For the detection of organic colouring matters, a portion of the ink should be strongly acidulated with hydrochloric acid. A blue colour, unaffected by the acid, but destroyed on adding bromine water or bleaching powder, shows the presence of indigo. If Prussian blue be present, the ink will probably turn brown on addition of soda, and the filtered liquid will give a deep blue precipitate with ferric chloride, after being acidified with hydrochloric acid. A black colour, not destroyed by acids or alkalies, nor bleached by chlorine or bromine, is pretty certain to be due to finely-divided carbon. An ink prepared with vanadate of ammonium and galls, is turned blue by acids, but is unaffected by alkalies. Its colour is altered but not bleached by chlorine. Aniline-black is not affected by alkalies, but is turned dark green by acids; bleaching powder renders it garnet-red. Logwood inks are turned red or yellow by hydrochloric acid, while those containing galls only are almost wholly decolorised by the same reagent.

Some inks have a great tendency to become mildewed; this may be prevented by a small addition of carbolic or salicylic acid.

COLOURED INKS do not usually contain tannic acid, and hence their discussion is out of place in this section; in many instances they are nothing but solutions of coal-tar dyes. The following examples will suffice to give a general idea of their composition :—



*Red.*—Brazil wood, with stannous chloride or cream of tartar and alum; cochineal or carmine dissolved in ammonia; aniline red.

*Blue.*—Prussian blue dissolved in oxalic acid; aniline blue.

*Violet.*—Aniline violet.

*Green.*—Acetate of copper and cream of tartar; chrome-alum.

**MARKING INK.**—These are all closely analogous in composition, and their assay requires no special description. They usually consist of nitrate of silver coloured with sap-green, ivory-black, indigo, &c.; or ammonio-nitrate of silver mixed with sodium carbonate, sometimes with sulphate of copper added. In Redwood's ink, tartrate of silver is substituted for the nitrate. Reade's ink is ammonio-tartrate of silver.

## CHRY SOPHANIC ACID.

**Rhein. Rhaponticin. Rhubarb yellow.**  $C_{15}H_{10}O_4$ .  
—Until recently, the formula of this substance was somewhat uncertain, but has been decided by the discovery that chrysophanic acid is reduced to methyl-anthracene,  $C_{15}H_{12}$ , when heated with zinc-dust. In many of its chemical relationships chrysophanic acid is allied to the aromatic group, and in fact appears to be homologous with chrysazin,  $C_{14}H_8O_4$ .

Chrysophanic acid is found in rhubarb, senna, the wall lichen (*Parmelia parietina*), and some other plants. It is most readily extracted by boiling the substance known in pharmacy as "Aroroba" or "Goa powder" with benzene or petroleum spirit, and filtering while hot. On cooling, the filtered liquid (concentrated, if necessary) deposits pale-yellow crystals, which may be purified by re-solution and crystallisation from hot benzene or rectified spirit. Goa powder is said to contain about 80 per cent. of chrysophanic acid, but according to a recent research by Liebermann and Siedler,\*

\* *Pharm. Journ.* 1879, May 3, page 896.

the body extracted from Goa powder by benzene is chrysarobin,  $C_{30}H_{26}O_7$ , chrysophanic acid being a product of its oxidation. Chrysarobin differs from chrysophanic acid by being insoluble in ammonia or very dilute soda, and by yielding with stronger alkali a yellow solution exhibiting a strong green fluorescence. On exposure to air, the liquid becomes red from formation of chrysophanic acid, which is precipitated on neutralising the solution with an acid, and may be washed, dried, and purified by crystallisation from petroleum spirit.

The proportion of chrysophanic acid contained in rhubarb is but small. According to Dragendorff, the presence of chrysophanic acid in a condition (free) extractable by cold petroleum spirit is a test of the quality of rhubarb. Good rhubarb yields a colourless extract even when left for several days in contact with petroleum spirit, while a rhapontic rhubarb yields an intensely yellow extract.

Chrysophanic acid forms golden-yellow scales or orange-red masses; it melts at  $162^{\circ}C.$ , and is partially volatilised at a higher temperature.

In water, chrysophanic acid is but slightly soluble; in hot alcohol it dissolves moderately well, the greater part separating on cooling. Chrysophanic acid is readily soluble in ether, chloroform, benzene, and petroleum spirit, forming yellow or brownish-yellow solutions. Acetic acid and amylic alcohol are also solvents of chrysophanic acid.

When treated with a solution of caustic alkali or ammonia, chrysophanic acid dissolves readily, forming a liquid which is pink when very dilute, and dark purplish-red in a more concentrated state. The chrysophanic acid is precipitated in yellow flakes on neutralising the alkaline liquid. A very small quantity of alkali suffices for the production of the red colour. If the red solution of chrysophanic acid in caustic alkali be evaporated to dryness, it turns violet and blue during the operation. The films deposited on the sides of the vessel especially exhibit this change of colour.

If a yellow solution of chrysophanic acid in ether, chloroform, benzene, or petroleum spirit be shaken with solution of soda, the colouring matter passes completely or partially into the aqueous liquid, which it colours pink or crimson. Ammonia gives the same reaction as soda with a solution of chrysophanic acid in ether or petroleum spirit, but does not extract the colouring matter from its solution in chloroform or benzene.

Chrysophanic acid is not acted on by dilute nitric acid, but the strong acid converts it into a red substance (tetra-nitro-chrysophanic acid, homologous with chrysamic acid). Strong sulphuric acid dissolves chrysophanic acid without change, and the colouring matter is re-precipitated on diluting the solution.

Chrysophanic acid possesses decided antiseptic properties, and has proved of great service in the treatment of some forms of skin disease. It is said to be somewhat uncertain in its action, a fact not improbably due to its adulteration, or possibly to an admixture of Liebermann's chrysarobin. When applied to the eyes, chrysophanic acid causes considerable irritation and decided dilatation of the pupil; the symptoms subside spontaneously in a few days.

The acid properties of chrysophanic acid are but feebly marked. It forms unstable barium and lead salts, which are decomposed even by carbonic acid. An ammoniacal solution of chrysophanic acid is precipitated lilac by acetate of lead and rose-coloured by alum.

Chrysophanic acid is said to produce purplish-brown stains on linen or cotton, which are only removable with difficulty, prolonged immersion of the fabric in a solution of bleaching-powder being the best mode of treatment. The author has not succeeded in producing these stains except in the presence of an alkali. A solution of chrysophanic acid in alcohol, acetic acid, or petroleum spirit, merely colours linen a light-yellow colour. On washing the stained

fabric with soap, the purplish-brown stain is readily developed.\*

An aqueous or alcoholic solution of chrysophanic acid does not dye silk or wool yellow.

Chrysophanic acid is liable to be adulterated with picric acid and other yellow colouring matters. Inorganic admixtures may be detected by igniting a portion of the sample. Picric acid, if present, will be detected by the yellow coloration the sample imparts to cold water; by the yellow crystalline precipitate produced on adding potassium carbonate to the aqueous or (better) alcoholic solution of the sample; and by immersing a piece of white wool in the hot aqueous solution; in presence of picric acid the wool will be dyed yellow. Aurin or rosolic acid may be detected in chrysophanic acid by treating the sample with chloroform or benzene, which dissolves the chrysophanic acid without affecting the admixture.

\* Evidently the way to avoid the production of chrysophanic acid stains on linen is to dissolve out the colouring matter and grease by means of benzene.



## PHENOLS.

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THE bodies known to chemists as phenols belong to the aromatic series, and are intermediate in character between acids and the true aromatic alcohols of which benzylic alcohol is the type. The probable difference in structure between the phenols and the aromatic alcohols is shown by the following formulæ:—

Phenols.		Aromatic Alcohols.	
Carbolic acid (phenol) . . .	} $\text{C}_6\text{H}_5.\text{OH}.$		
Cresylic acid (cresol) . . .			
	} $\text{C}_6\text{H}_4(\text{CH}_3).\text{OH}.$	Benzyl alcohol .	$\text{C}_6\text{H}_5.\text{CH}_2\text{OH}.$
Phlorol . . . .			
	} $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5).\text{OH}.$	{ Xylyl alcohol (xylol) . . .	} $\text{C}_7\text{H}_7.\text{CH}_2\text{OH}.$
Dimethyl-phenol .			
	} $\text{C}_6\text{H}_3(\text{CH}_3)_2.\text{OH}.$	{ Cymyl alcohol (cymol) . . .	} $\text{C}_9\text{H}_{11}.\text{CH}_2\text{OH}.$
Thymol . . . .			
	} $\text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_2.\text{OH} (?)$		

According to these formulæ, cresylic acid has the constitution of a methyl-carbolic acid, while its isomer benzyl-alcohol is phenyl-wood-spirit.

Of the above bodies, only the phenols are of such importance as to require further description.

GUAIACOL and CREASOL have the constitution of oxy-phenols, and are considered on page 320, *et seq.*, in the article on creasote.

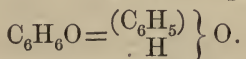
PYROCATECHIN,  $\text{C}_6\text{H}_6\text{O}_2$ ; RESORCIN,  $\text{C}_6\text{H}_6\text{O}_2$ ; and ORCIN,  $\text{C}_7\text{H}_8\text{O}_2$ , also have the composition of oxy-phenols, but require no special description.

PYROGALLOL,  $\text{C}_6\text{H}_6\text{O}_3$ , which may be regarded as a dioxy-phenol, is described on page 281, under the name of pyrogallic acid.

**CARBOLIC ACID.**

**Phenic Acid; Phenol;\* Phenylic Hydrate; Phenyl Alcohol; Coal-Tar Creasote.**

*French*—Acide Phenique.



Pure carbolic acid is a colourless crystalline solid, melting at  $42.2^\circ \text{C.}$  ( $=108^\circ \text{F.}$ )  $\dagger$  to a colourless, limpid fluid, slightly heavier than water. Carbolic acid boils, when pure, at  $182^\circ \text{C.}$ , and distils without decomposition. The crystals readily absorb moisture from the air, whereby their fusing point is lowered, owing to the formation of a hydrate of the formula  $\text{C}_6\text{H}_6\text{O}, \text{H}_2\text{O}$ , containing 16.07 per cent. of water and melting at  $17.2^\circ \text{C.}$  ( $=63^\circ \text{F.}$ ). In very moist air this hydrate absorbs still more water, and the product remains fluid at a still lower temperature. When water is gradually added to carbolic acid as long as it continues to be dissolved, the resultant liquid contains about 27 per cent. of water (by weight), and thus approximates closely to the composition  $\text{C}_6\text{H}_6\text{O}, 2\text{H}_2\text{O}$ , which requires 27.7 per cent. of water. If the liquid so obtained be really a compound, it is one of the weakest nature, for on agitating it with four volumes of benzene the carbolic acid is dissolved and the water wholly separated. The liquid hydrous carbolic acid obtained as above is readily frozen by the cold resulting from the mixture of  $2\frac{1}{2}$  fluid ounces of strong hydrochloric acid with 4 ounces of crystallised sulphate of sodium.

Liquid hydrous carbolic acid dissolves in about 11.1 times its measure of cold water. This corresponds to a solubility of 1 part by weight in 10.7 for the absolute acid, the saturated solution containing 8.56 per cent. of real phenol. Although aqueous

\* The name "phenol" is applied generically to bodies of the aromatic series having properties allied to true alcohols and also to acids. The series of which carbolic acid is the lowest member has the general formula  $\text{C}_n\text{H}_{2n-6}\text{O}$  (see p. 302).

$\dagger$  Specimens of carbolic acid having a lower melting point than  $42^\circ \text{C.}$  contain cresylic acid or water.

solutions of carbolic acid do not redden litmus, carbolic acid is much more soluble in weak alkaline solutions than in pure water. With equivalent amounts of the strong bases it forms definite compounds; the potassium and sodium salts are readily soluble in water, and are not decomposed on dilution.

Carbolic acid is miscible in all proportions with alcohol, glacial acetic acid, and glycerin.

*Absolute* carbolic acid is miscible in all proportions with ether, benzene, carbon disulphide, and chloroform. When *aqueous* carbolic acid is shaken with excess of either of these solvents, the phenol dissolves and the contained water is separated.

In cold petroleum spirit, carbolic acid is but slightly soluble.\*

The taste of carbolic acid is biting, but at the same time sweet. The odour is usually strong and characteristic, but both smell and taste are much less marked in very pure specimens than in the crude article.†

Commercial carbolic acid often turns red in the light; the cause is uncertain.

Phenol coagulates albumin, is a powerful antiseptic, acts as a caustic on the skin, and is powerfully *poisonous*. It appears to act on the system by paralysing the nerve centres. The effect of even momentary contact of the strong acid with any considerable surface of the lower part of the body is usually fatal, but it has often been applied to the arms with comparative impunity.

Strong carbolic acid dissolves dry gelatin completely, but it coagulates it when added to its aqueous solution.

Indigo-blue is soluble in hot phenol, and may be obtained in crystals on cooling.

\* For details of its behaviour, see page 317. The statements here made respecting the solubility of carbolic acid in water and other solvents are all the result of my personal experience. The details of the investigation are published in the *Analyst*, iii. 319, and in the *Year Book of Pharmacy*, 1878, page 575.

† The addition of four drops of French oil of geranium to each fluid ounce retains the acid in a liquid condition, and communicates an agreeable smell.

Carbolic acid is converted by the action of chlorine and bromine into trichloro- and tribromo-phenol. Nitric acid acts on it with formation of mono- di- or tri-nitrophenol; the last of these is identical with picric acid. (See page 327.) Concentrated sulphuric acid converts carbolic acid into sulpho-phenic acid. (See page 325.)

Phenol is a constituent of *castoreum*, B.P., and is formed in many reactions. In practice it is always obtained from coal-tar.\*

For many years phenol was confounded with creasote, a body of very similar properties extracted from beechwood tar. The confusion was increased by the unacknowledged substitution of one substance for another in commerce, and by the presence, both in coal- and in wood-tar, of homologues of the substances originally known as carbolic acid and creasote.

Thus, there have been obtained

FROM COAL-TAR—

Carbolic acid, phenol, or phenylic hydrate,  $C_6H_6O$ ,  
boiling at  $182^{\circ} C$ .

Cresylic acid, cresol, or cresylic hydrate,  $C_7H_8O$ ,  
boiling at  $198^{\circ}$  to  $203^{\circ} C$ .

Xylenol, dimethyl-phenol, or xilylic hydrate,  $C_8H_{10}O$ ,  
boiling at  $211^{\circ}$  to  $213^{\circ} C$ .

\* For the following details of the manufacture of carbolic acid, and for other valuable information in this section, I am indebted to Mr Charles Lowe. 20 tons of gas-tar are introduced into a retort and distilled. The first 200 gallons of "light benzols" are of no use for the extraction of carbolic acid. When that amount of distillate has passed over, the next 600 gallons are collected separately. For each 200 gallons of these oils,—having a density of 1.0 to 1.005, 30 gallons of caustic soda solution of 1.34 sp. gr. are added after dilution to 150 gallons, and the oils then agitated with the solution for two hours. The mixture is next allowed to settle for four hours, when the alkaline solution is drawn off and neutralised with sulphuric acid. The crude carbolic acid rises to the surface and is skimmed off, and is then allowed to settle in tanks for several days, when it is ready for casking. The caustic soda used must be free from nitrates.



## FROM WOOD-TAR \*—

Guaiacol, oxy-cresol,  $C_7H_8O_2$ , boiling at  $200^{\circ} C$ .

Creasol,  $C_8H_{10}O_2$ , boiling at  $217^{\circ} C$ .

Methyl-creasol,  $C_9H_{12}O_2$ , boiling at  $214^{\circ}$  to  $218^{\circ} C$ .

Phlorol,  $C_8H_{10}O$ , boiling at  $219^{\circ} C$ .

## REACTIONS OF CARBOLIC ACID.

The following reactions are in most cases common to carbolic and cresylic acids. They do not require that the substance should be in a concentrated state, but are applicable to the aqueous solution. They have all been verified by the author. Various other reactions of carbolic acid are described in the sections on cresylic acid and creasote (pages 317 and 321).

1. When a drop of a dilute aqueous solution of carbolic acid is added to a few drops of a solution of 1 part of molybdic acid in 10 of concentrated sulphuric acid, contained in a porcelain crucible, a yellowish-brown coloration is produced, which rapidly changes to purple, the latter tint being tolerably permanent. Warming the mixture to about  $50^{\circ} C$ . greatly assists the reaction, but a higher temperature must be avoided. As this delicate reaction depends on the deoxidation of the molybdic acid, a great many substances interfere with this test.

2. Ferric chloride (avoiding excess) gives a fine violet colour, by which 1 part of phenol in 3000 of water can be detected. The presence even of neutral salts often interferes with the reaction.

3. If an aqueous solution of phenol be gently warmed with ammonia and solution of sodium hypochlorite † (avoiding excess) a deep blue colour is obtained, which is lasting, but turns to red on addition of acids. Solutions containing 1 of phenol in 5000 of water react well when 20 c.c. are employed. Much smaller quantities give the reaction after a time.

4. If 20 c.c. of a dilute phenol solution be boiled with 5 or

\* Carbolic and cresylic acids are also obtainable from pine-wood tar.

† Sodium hypochlorite is prepared by precipitating a clear aqueous solution (prepared in the cold) of bleaching powder (chloride of lime), with a slight excess of sodium carbonate, and filtering from the precipitated  $CaCO_3$ .

10 drops of Millon's reagent,\* and nitric acid added drop by drop to the hot solution, until the precipitate is redissolved, the mixture assumes a fine red colour, which is permanent for several days. The reaction is exceedingly delicate, but is not peculiar to phenol.

5. One of the most delicate and satisfactory tests for phenol in dilute solution is that with bromine water, the addition of which occasions the formation of a crystalline precipitate of tribromophenol. In extremely dilute solutions the precipitate is only produced slowly. In twenty-four hours, a solution containing but  $\frac{1}{60.000}$  of phenol gives the reaction.

TRIBROMOPHENOL,  $C_6H_3Br_3O$ , appears under the microscope in the form of fine stellated needles. It has a peculiar smell, and is insoluble in water and acid liquids, but dissolves in alkalis, ether, and absolute alcohol. A very small quantity of water completely precipitates it from its alcoholic solution. The reaction with bromine has been employed to demonstrate the effect of a gas-works on the water of the neighbouring wells.

TRIBROMOCRESOL,  $C_7H_5Br_3O$ , is a liquid at ordinary temperatures, but in other respects closely resembles the phenol derivative.

Similar precipitates are produced by the action of bromine on solutions of creasote, oxybenzoic acid, thymol, and various alkaloids.

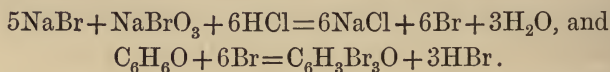
**Determination and Assay of Carbolic Acid.** — A method of determining carbolic acid by weighing the bromine derivative is described on page 315, but its bulk and its volatility at  $100^\circ C.$  are serious difficulties. On the other hand, Koppeschaar† has found that the bromine reaction may be made available for the accurate volumetric determination of phenol by proceeding in the following manner:—

A weighed quantity of the sample is dissolved in water, and

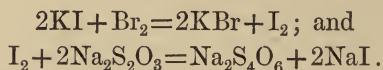
\* Prepared by dissolving mercury in fuming nitric acid, boiling, and diluting the solution with two volumes of water.

† *Zeitschr. f. Anal. Chem.* iii. 1876, pp. 233-245.

a volume of the solution containing 0·1 gramme of the original sample is taken for analysis. This is placed in a stoppered flask holding 250 c.c. 70 c.c. of normal caustic soda solution are treated with bromine gradually till permanently yellow, and then boiled until the excess of bromine has been driven off and the colour has disappeared. The liquid (which contains  $5\text{NaBr} + \text{NaBrO}_3$ ) is cooled and added to the phenol solution, being immediately followed by 5 c.c. of pure concentrated hydrochloric acid. The stopper is at once inserted, and the flask well shaken for some time. The following reactions occur :—



Any excess of bromine liberated in the first reaction above that necessary for the second, will exist in a free state. Its amount is found by causing it to react on potassium iodide and then ascertaining the amount of free iodine by titration with standard solution of sodium thiosulphate (hyposulphite). Thus,—



After the flask has stood 15 or 20 minutes, a solution of about 1·25 grammes of pure potassium iodide (free from iodate) is added, the stopper replaced, the whole shaken, and then left at rest for a short time. The contents and washings of the flask are then transferred to a beaker or porcelain basin, a little starch solution added, and decinormal thio-sulphate (hyposulphite) run in from a burette till the blue colour disappears. The purer the sample of phenol the less bromine will remain free, the less iodine will be liberated, and hence the less hyposulphite will be required.

The amount of bromine neutralised by 70 c.c. of normal soda is 0·560 grammes, the same amount being subsequently set free on addition of hydrochloric acid. 0·1 gramme of pure phenol would react on ·4068 grammes of this, leaving ·1532

grammes of bromine in excess. This would liberate enough iodine to decompose 19.15 c.c. of decinormal thiosulphate. Each c.c. used *in excess of this amount*, indicates .00197 of impurity in the .1 gramme of sample taken, or 1.97 per cent.

Koppeschaar prepares the bromine solution of unknown strength, and then titrates it with potassium iodide and thiosulphate. The above method of preparing it is simpler and equally satisfactory. If desired, a larger quantity of standard soda may be neutralised with bromine, and a blank analysis made on a portion of it by adding hydrochloric acid and potassium iodide solution, and titrating with thiosulphate. Koppeschaar's test experiments gave results varying from 99.2 to 99.5 of phenol found for 100 taken.

Cresylic acid may be determined in a similar manner, but, owing to its higher atomic weight, the results must be multiplied by 1.106 to get the true amount present.

Degener titrates direct with bromine water, using KI and starch as an indicator. The strength of the bromine water is ascertained immediately previously.

For the approximate assay of crude carbolie acid, G. Leube\* shakes 5 grammes of the sample with 100 grammes of water, allows tar, &c., to settle, takes 10 c.c. of the clear solution and adds 10 drops of a 10 per cent. solution of ferric chloride in water. The depth of tint is compared with that obtained from freshly prepared aqueous solutions of carbolie acid of known strength.

When carbolie or cresylic acid is treated with strong sulphuric acid a conjugated acid is produced, which forms soluble barium and lead salts. It has therefore been proposed to determine carbolie acid by heating the sample with sulphuric acid, treating the product with excess of oxide of lead or carbonate of barium, and subsequently precipitating the dissolved lead or barium sulphophenate by sulphuric acid. Some test experiments made by the author on pure carbolie and cresylic

\* *Dingl. Polyt. ceii.* 308 ; and *Journ. Chem. Soc.* 1872, page 266.



acids, showed that the process was useless, owing to the tendency to the formation of di-sulphophenic acid by the use of the necessary excess of sulphuric acid. If less sulphuric acid be employed some phenol is left unconverted.

Much of the liquid carbolie acid of commerce is extremely impure, consisting chiefly of cresylic acid. In addition to this it is often largely adulterated with neutral tar-oils, of little or no value as antiseptics.

For the determination of the tar-oils the following simple method may be used:—Introduce 5 c.c. or 50 fluid grains of the sample into a graduated tube, and add gradually, noting the effect produced, twice its volume of a solution of caustic soda free from alumina, containing 9 per cent. of NaHO. Then close the tube and agitate well. The coal-tar acids will be completely dissolved by the alkaline liquid; whilst, on standing, the neutral oils will form a separate stratum above or below the other, according as the admixture consisted of the light or heavy “oil of tar.” By the volume occupied by the oily stratum the extent of the adulteration is at once indicated. After noticing whether the tar-oils are light or heavy, a volume of petroleum spirit equal to that of the sample taken may be advantageously added. Its employment facilitates the separation of the oily stratum, and renders the reading of its volume more easy and accurate. Of course, the volume of petroleum spirit used must be deducted from that of the total oily layer.\*

The specific gravity of crude carbolie acid at  $15.5^{\circ}$  C. ( $=60^{\circ}$  F.), should be between 1.050 and 1.065. If lighter, it is suspicious. In presence of light tar-oil the density is often as low as 1.040 or 1.045.

The following method for the assay of crude carbolie acid, with the view of approximately determining the proportions

\* This modification of the soda test was first described by me in the pages of the *Analyst*, 1878, page 288. It was suggested by a test of Hager's, but the way in which he applies it leads to inaccurate results.

of its constituents, was kindly communicated to the author by Mr Charles Lowe:—

1000 grains measure of the sample are placed in a retort (without any special condensing arrangement), and distilled, the liquid which passes over being collected in graduated tubes. Water first distils, and is followed by an oily fluid. When 100 fluid grains of the latter have been collected, the receiver is changed. The volume of water is then read off. If the oily liquid floats on the water, it contains light oil-of-tar. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50 per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid, and when it measures 625 grains the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 625 grains measure of anhydrous acid contains variable proportions of carbolic and cresylic acid. These may be approximately determined by ascertaining its solidifying point, which should be between 60° and 75° F. (15·5° and 24° C.) Having ascertained this temperature, a mixture of pure carbolic and cresylic acids is made in such proportions as to have the same solidifying point. This must be adjusted by trial, or a series of standard specimens may be prepared. The exact point of solidification can be more sharply read if a minute fragment of crystallised carbolic acid be added to induce the commencement of the change of state; or the sample may be solidified, and the liquefying point noted. As excess of cresylic acid prevents crystallisation, it is evident that in some cases a second fractional distillation should be resorted to, the process being arrested when the thermometer rises to 190° C.

**Toxicological Detection of Carbolic Acid.**—This is not unfrequently necessary, owing to the numerous instances in which poisoning has ensued from its accidental administration internally. In such cases the mouth and œsophagus are

usually white, soft, and corroded, but are sometimes found hardened and shrivelled.

The stomach is usually white, contracted, thickened and shrivelled, but sometimes intensely congested, with destruction of the mucous membrane; occasionally no abnormal appearance is observable. The intestines are usually thickened and congested. The bladder is generally quite or very nearly empty, any urine having a dark colour.

In testing animal matters for carbolic acid, the smell is a most valuable indication. For the recognition of the poison, the suspected matters are cut up and well shaken with water acidulated with sulphuric acid. The liquid is then distilled, and the tests for carbolic acid applied to the distillate. (In examining urine, the addition of acid should be omitted.) The tests of most service are the smell, the reactions with ferric chloride, sodium hypochlorite, and bromine, and the property of coagulating albumin.

Carbolic acid may often be conveniently concentrated by shaking the fluid to be tested (*e.g.*, urine) with sulphuric acid and ether, separating the ethereal layer, and examining the residue of its evaporation by the tests for carbolic acid.

**Carbolic Acid Powders** are disinfecting powders, containing more or less crude carbolic acid. In some cases the base of the powder is slaked lime, but the resultant "carbolate of lime" is of little value for antiseptic purposes. "Macdougall's Disinfecting Powder" is made by adding a certain proportion of crude carbolic acid to an impure sulphite of calcium, prepared by passing sulphurous acid gas over ignited limestone.\* The product often contains free lime. "Calvert's Carbolic Acid Powder" is made by adding carbolic acid to the siliceous residue resulting from the manufacture of sulphate of aluminium from shale.

The relative antiseptic values of different carbolic powders

\* For the analysis of the bases of Macdougall's and Calvert's carbolic powders, see a paper of mine in the *Analyst*, 1878, vol. iii. page 286.

can be tested by mixing 25 grains of each sample with 1 ounce of flour. Add gradually to each mixture 10 ounces of water, and stir well in the cold; then bring the liquid to the boil, pour the resultant pastes into open vessels, and leave them freely exposed to the air. Note the length of time which elapses in each case before the formation of mildew occurs, and on which paste the growth takes place most easily and rapidly.

For the determination of the percentage of crude acid contained in siliceous carbolic powders, the following simple process may be used:—

Introduce 1000 grains or 100 grammes of the powder into a tubulated glass retort, and heat the vessel over a flame. Crude carbolic acid distils over, and may be collected in a graduated tube. The process is continued as long as anything passes over. The heat should be pushed to dull redness, and the contents of the retort occasionally shaken towards the end of the process. On standing, the aqueous portion of the distillate separates from the oily liquid, and the volume of the latter may be read off. In two test experiments the author obtained 14·2 c.c. of crude acid for 15 c.c. added. This correction may be applied in accurate experiments. The real weight of the distillate is about  $\frac{1}{20}$  greater than is indicated by the volume, owing to its density being greater than that of water.

The same process can be applied, though less accurately, to Macdougall's Disinfecting Powder.

Good carbolic acid powders contain 12 or 15 per cent. of crude carbolic acid, but they are liable to lose 1 or 2 per cent. by volatilisation. The quality of the crude carbolic acid obtained by the distillation process can be conveniently tested by the method with solution of soda described on page 310. Some powders in the market contain but 5 or 6 per cent. of total oils, of which less than half is really carbolic and cresylic acids, the remainder being worthless tar-oil.



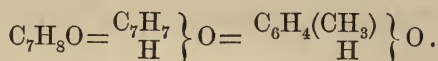
The above distillation process does not answer for the assay of carbolic powders made with lime, but an approximate assay of "carbolate of lime" and other alkaline carbolic powders may be effected as follows:—50 or 100 grammes of the sample are mixed in a large Wedgwood mortar with 10 per cent. of water. Strong sulphuric acid previously diluted with an equal bulk of water is then added very gradually, a few drops only at a time. After each addition the whole is well mixed together with a pestle. The addition of the acid, which should extend over some hours, to avoid sensible rise of temperature, is continued until a minute fragment of the well-mixed contents of the mortar shows an acid reaction when placed on a piece of litmus paper and moistened with water. If the mixture be pasty, sufficient sand is mixed with it to cause it to granulate, and the mortar is then covered up and left for some hours. By proceeding in the above manner, the whole of the lime combines with the sulphuric acid and water to form gypsum, while the carbolic acid is liberated. The contents of the mortar are then transferred to a retort and subjected to dry distillation in the same way as a siliceous powder. The oily portion of the distillate will contain any neutral coal-oils present in the sample, and the quantity of such matters may be found by treating it with soda as described on page 310. A very considerable proportion of the coal-tar acids is liable to remain in solution in the aqueous part of the distillate, and must be determined in an aliquot portion of that liquid by bromine or ferric chloride, and the quantity so found added to that dissolved by soda from the oily layer. When it is desired merely to assay the powder for coal-tar acids, 5 grammes of the sample may be triturated with a slight excess of dilute sulphuric acid, the liquid filtered, and the bromine process applied to the filtrate. An accurate and simple method of assaying carbolate of lime is still a desideratum. It might possibly be effected by decomposing the powder with a slight excess of acid, agitating the

liquid with ether, removing the ethereal layer, concentrating it by spontaneous evaporation, and observing the loss of bulk occasioned by treating it with soda solution.

**Carbolic Acid Soap** is made by incorporating carbolic acid with the soap during the process of manufacture. The best qualities are made to contain 10 per cent. of the crystallised acid, but in the inferior kinds the acid is chiefly cresylic. The acid is free, and the soap will readily lose 2 or even 3 of the 10 per cent. added. The following process, communicated by Mr Charles Lowe, suffices to determine the contained acid, and to ascertain whether the crystallised or crude article was employed:—

50 fluid grains of solution of caustic soda of 1·345 sp. gr. are diluted to 1000 fluid grains by means of water. In this liquid 100 grains of the soap are dissolved by the aid of heat. 1000 fluid grains of a saturated solution of common salt are next added, and the liquid again heated and allowed to cool. The precipitated soap is filtered off, and washed with strong brine. The filtrate is slightly acidified by hydrochloric acid and bromine water added in sufficient quantity to render the liquid permanently yellow. Warm the liquid sufficiently to melt the precipitate to an oil, and then allow it to cool. A little more precipitate will crystallise out, but the bulk forms a hard mass, which may be removed, carefully dried, and weighed. If crude carbolic acid containing much cresylic acid were used in the manufacture of the soap, the bromine precipitate forms a sticky mass, owing to the liquid nature of the tribromocresol. If desired, the bromine can be employed volumetrically, as described on page 308.

**Carbolates** are produced on addition of carbolic acid to strong bases. They give off carbolic acid when heated in the solid state, or when boiled with moderately dilute sulphuric acid. With nitric acid they yield picrates. Carbolates give a reddish-violet colour with ferric chloride. The assay of calcium carbolate is described on page 314.

**CRESYLIC ACID.****Cresol. Cresylic Hydrate. Cresylic Phenol.**

This substance is contained very largely,—often constituting far the greater part,—in the crude carbolic acid obtained from coal-tar. It may be determined by the same methods as those employed for carbolic acid, and is repeatedly referred to in the section treating of that body.

CRESYLIC ACID FROM COAL-TAR has a density of about 1.044. It closely resembles carbolic acid, but is liquid, far less soluble in water, and boils at a higher temperature than the latter. The boiling point of commercial cresylic acid is very variable, as it contains more or less of carbolic acid and higher homologues. At least two isomeric varieties of cresol, having slightly different boiling points, are contained in coal-tar. A cresol solid at ordinary temperatures has been obtained. Samples of commercial carbolic acid containing much cresylic acid remain fluid at ordinary temperatures (even when anhydrous), and are less soluble in water and alkaline liquids than pure carbolic acid (see next page). Cresol resembles phenol in its reactions with ferric chloride, and, when acted on by strong nitric or sulphuric acid, gives similar, but not identical, products with those yielded by carbolic acid. With bromine it produces a similar body, but the tri-bromo-cresol is liquid at ordinary temperatures, whereas tri-bromo-phenol is solid. Cresylic acid possesses antiseptic properties in even a greater degree than carbolic acid. The following table shows the chief differences of analytical value existing between carbolic and cresylic acids. The statements have been personally verified by the author upon a sample of Calvert's No. 1 Carbolic acid, and a cresylic acid prepared purposely by fractional distillation of a sample of Calvert's No. 5 Carbolic acid.

*Carbolic Acid.**Cresylic Acid.*

1. Melting point.	Solid at ordinary temperatures; liquefied by addition of water; both absolute and hydrated acid solidified by freezing mixture.	Liquid at ordinary temperatures; neither absolute nor hydrous acid is solidified by freezing mixture.
2. Boiling point.	182° C.	198° to 203° C.
3. Solubility of hydrous acid in cold water.	1 volume in 11.	1 volume in 29.
4. Solubility in strong solution of ammonia (sp. grav. 880).	Completely and readily soluble in equal volume; solution not precipitated by addition of less than 1½ volumes of water.*	Almost insoluble; requires upwards of 16 volumes; then forms crystalline scales.
5. Reaction with solution of caustic soda (free from alumina), containing 6 per cent. NaHO ( <i>i.e.</i> , 6 grammes to 94 c.c. of water).	Completely soluble in equal volume. Addition of the alkali solution, even up to 6 volumes, causes no change.	Insoluble in small proportions. With large excess it disappears, and forms crystalline scales.
6. Reaction with solution of caustic soda, containing 9 per cent. NaHO ( <i>i.e.</i> , 9 grammes to 91 of water).	Completely and readily soluble in equal volume. On addition of any proportion of water up to 7 volumes, the liquid remains clear, but is precipitated by 8 measures of water. Soluble in 2 measures of soda, and not precipitated by less excess than 5 or 6 measures.	Soluble in equal volume, but precipitated by adding a few drops of water, the original volume separating when water is added to 1 measure. The solution in soda is reprecipitated when the alkali solution is added to the extent of 3½ measures.
7. Reaction with petroleum spirit.	Absolute acid is miscible with hot petroleum spirit in all proportions. Miscible with only ½ volume cold petroleum spirit, precipitated by greater proportion. With 3 volumes petroleum spirit, bulk unchanged; upper layer contains carbolic acid, which crystallises out on sudden cooling by freezing mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solution in 3 measures of petroleum spirit.
8. Behaviour with glycerin of 1.258 sp. gr.	Miscible in all proportions. One measure of carbolic acid with an equal volume of glycerin is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 volumes of water being the maximum for a sample containing 25 per cent. cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerin, is completely precipitated by 1 measure of water.

\* One part of carbolic acid and three of cresylic acid dissolve in an equal measure of ammonia, but the liquid is precipitated on adding a few drops of water.

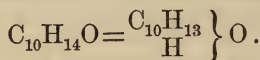


From these reactions it will be seen that cresylic acid is less soluble in water, ammonia, glycerin, and solution of soda than is the case with carbolic acid, but it is more soluble in petroleum spirit. Although the above tests suffice for the detection of considerable proportions of cresylic acid in admixture with carbolic acid, they afford no basis for its quantitative determination, except of the roughest kind. The only available means of even approximately determining the proportion of cresylic acid present in samples of crude carbolic acid is that described on page 313.

The antiseptic properties of cresylic acid are even more strongly marked than those of carbolic acid.

### THYMOL.

**Thymic Acid. Cymylic Phenol. Thymylic Hydrate.**



This substance is the camphor or stearoptene of thyme oil, and is also obtained from the volatile oils of horse-mint and ajowan.

Thymol is homologous with carbolic and cresylic acids, and closely resembles them in its general properties. It is a powerful antiseptic, its preservative power being ten times as great as carbolic acid according to Bucholz, and four times as great according to Willmott. It acts as a caustic on the lips and mucous membrane, but does not irritate the skin like carbolic acid.

Thymol is a solid crystalline substance, with feeble aromatic smell and burning taste. Thymol melts at 44° C., and does not readily re-solidify unless touched by a solid body or a crystal of thymol. It boils at 220° to 230° C. Solid thymol is slightly heavier than water, but in the fused state it is rather lighter; the density appears to be somewhat variable. In water, thymol is scarcely soluble, requiring about 1000 parts for solution. Even this weak solution is powerfully antiseptic.

Rectified spirit dissolves its own weight of thymol, the greater part separating again on dilution. A solution of 4 grains of thymol to the fluid ounce of spirit is miscible with water in all proportions. Thymol is very sparingly soluble in glycerin, requiring 120 parts for solution. The liquid is precipitated by an equal measure of water, but is perfectly miscible with four measures. The solution so obtained is a useful lotion.

Thymol is readily soluble in ether and in strong acetic acid. When thymol and camphor are triturated together, a syrupy liquid is obtained, which is readily miscible with vaseline and similar preparations. Milk is said to dissolve 10 per cent. of thymol. Thymol is insoluble in small quantities of alkaline liquids, but dissolves in presence of an equivalent amount of soda (40 of soda to 150 thymol), forming a soluble compound, which is decomposed by acids with separation of the thymol. With strong sulphuric acid, thymol forms a sulpho-acid.

Thymol is distinguished from carbolic acid by its slight solubility in water, glycerin, and alkaline solutions. It is best separated by fractional distillation.

Thymol is extracted from the essential oil of thyme, horse-mint, or ajowan, by agitating it with an equal measure of a solution of 1 part of caustic soda in 5 of water. The aqueous layer is removed and treated with excess of acid, when the thymol separates as an oily layer. A better plan is to expose the crude oil to a temperature of  $0^{\circ}\text{C}$ ., when the thymol crystallises out. It may be purified by recrystallisation from alcohol.

**Essential Oil of Thyme** consists chiefly of a mixture of thymol with the hydrocarbons thymene,  $\text{C}_{10}\text{H}_{16}$ , and cymene,  $\text{C}_{10}\text{H}_{14}$ . When the oil is distilled, thymene passes over between  $160^{\circ}$  and  $165^{\circ}$ , and the cymene between  $170^{\circ}$  and  $180^{\circ}\text{C}$ .; the thymol is much less volatile, and passes over towards the end of the distillation. Much of the oil of thyme of commerce consists merely of thymene and cymene, the thymol having been already extracted.

The oil of thyme may be assayed for thymol by the process with alkali used for the extraction of thymol.

The presence of turpentine in oil of thyme may be detected by adding a few grains of iodine to five or six drops of the oil. In presence of turpentine a lively reaction at once ensues, with considerable rise of temperature and disengagement of vapours. Thyme oil itself gives a slight reaction after a time.

Oil of thyme is colourless when freshly distilled, but becomes deep red on keeping. It has a density of  $\cdot 87$  to  $\cdot 90$ .

## CREASOTE.

**Kreozote.**—This name is properly applied only to the product of the distillation of wood-tar, but the term has also been employed to denote the mixture of crude phenols obtained by the distillation of coal-tar. Hence crude carbolic acid is sometimes known as “coal-tar creasote.” (See page 305.)

WOOD-TAR CREASOTE is not a definite substance, but a very variable mixture of several phenol-like bodies. Of these, the chief are—

**Guaiacol** (or oxy-cresol),  $C_7H_8O_2$ , boiling at  $200^\circ C.$ ,\* and **Creasol**,  $C_8H_{10}O_2$ , boiling at  $217^\circ C.$

Smaller quantities of phlorol ( $C_8H_{10}O$ ), methylcreasol ( $C_9H_{12}O_2$ ), and other bodies are also present. Carbolic and cresylic acids have also been met with in pine-wood tar. In Rhenish creasote, guaiacol predominates.†

Guaiacol is not soluble in glycerin.

Morson's English creasote is prepared from “Stockholm tar.” A sample examined by the author boiled at about  $217^\circ C.$ , and thus consisted chiefly of creasol.

Wood-tar creasote closely resembles the coal-tar acids. It

\* According to some observers, guaiacol boils at  $210^\circ C.$

† Bräuninger (*Journ. Chem. Soc.* 1878, ii. p. 146) examined a sample of Rhenish beechwood creasote of sp. gr.  $1\cdot 04$ , which distilled between  $180^\circ$  and  $216^\circ C.$ , the greater part (guaiacol) boiling at  $199^\circ$  to  $203^\circ C.$  The sample is stated to have contained a trace of carbolic acid, and  $1\cdot 3$  per cent. of cresylic acid.

is sparingly soluble in, and slightly heavier than, water, has a peculiar smoky taste and smell, and is a powerful antiseptic. It preserves animal matters without causing disintegration as carbolic acid is liable to do, and is less powerfully caustic than the latter substance. Like absolute cresylic and carbolic acid, it is miscible in all proportions with alcohol, ether, acetic acid, chloroform, carbon disulphide, and benzene. Its reactions with sulphuric acid, nitric acid, bromine, and gelatin are also very similar to those of carbolic acid.

Wood-tar creasote is often adulterated with, or wholly substituted by, crude carbolic acid. The reactions of cresylic acid resemble those of creasote still more closely than do those of pure carbolic acid, and hence the distinction between wood creasote and the crude product from coal-tar is rendered somewhat troublesome. This is especially the case when, as frequently happens, the substances are in actual admixture, the distinction between them when separate being comparatively easy.

The following reactions are the personal experience of the author :—

1. Morson's creasote is practically insoluble in strong ammonia, or in 6 per cent. soda. It is also insoluble in any smaller proportion than two volumes of 9 per cent. soda, and is partially reprecipitated when more than  $3\frac{1}{2}$  volumes of the solvent are added.

2. Creasote is sharply distinguished from the coal-tar acids by its insolubility in Price's glycerin (sp. gr. 1.258), whether one, two, or three times its volume of that liquid be employed. A mixture of equal parts of Morson's creasote and the highly cresylic coal-tar product known as "Calvert's No. 5 carbolic acid" dissolves in an equal measure of glycerin. The liquid is not affected by a drop or two of water, but a further addition causes precipitation. A mixture containing  $\frac{1}{4}$  of creasote to  $\frac{3}{4}$  of coal-tar acids dissolves in an equal measure of glycerin, and is not precipitated by less than  $1\frac{1}{4}$  measures of water.



3. Creasote is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose. Shaken with half its measure of *Collodium*, B. P., Calvert's No. 5 acid coagulates the gun-cotton to a transparent jelly, best observed by inclining the tube and causing the liquid to flow gently from one end to the other. Creasote does not precipitate the nitrocellulose from collodion, but mixes perfectly with the ethereal solution. Addition of much creasote to a mixture of collodion and a coal-tar acid causes a re-solution of the precipitated nitrocellulose. When a mixture of equal volumes of creasote and Calvert's No. 5 acid is shaken with half its measure of collodion, decided signs of precipitation are observed. With two-thirds of the coal-tar acids to one-third of creasote, the precipitation of nitrocellulose is very marked.

4. The addition of one drop of a 10 per cent. aqueous solution of ferric chloride to 15 c.c. of an aqueous solution of a coal-tar acid, causes a permanent violet-blue coloration. When creasote is similarly tested a blue colour results, which almost instantly changes to green and brownish-yellow.\* The test is useless for the recognition of coal-tar acids in admixture with creasote.†

\* For further information respecting the reaction with ferric chloride, see *Year-Book of Pharmacy*, 1877, p. 43, and *Journ. Chem. Soc.*, xxxii. 515.

† Other distinctive tests for creasote and carbolic acid are to be found in the books, but are almost worthless in practice. Thus their reactions with bromine, sulphuric acid, sulpho-molybdic acid, and nitric acid, are far too much alike to be of service for distinguishing between them. It has been stated that creasote differed from carbolic acid in its power of rotating a ray of polarised light. I redistilled a sample of Morson's creasote to obtain it colourless, and carefully tried this test, expecting to find in it a possible means of determining the creasote in a mixture, but the rotatory power of creasote proved so exceedingly weak as to be quite worthless for the intended purpose, or even as a qualitative test. It is, however, quite possible that different samples of creasote may exhibit considerable differences in this respect, but if so, the test is valueless for quantitative purposes, and the problem is not so much to detect wood-creasote as to recognise an admixture of the coal-tar acids. I am also unable to confirm the statement that creasote gives a solid deposit when kept for some hours at the temperature of boiling water. I have not obtained satisfactory results by the reaction of an alkaline solution of the substances with hydrochloric acid and pine-wood, or with a solution of iodine in iodide of potassium.

From the foregoing reactions it will be seen that carbolic acid, cresylic acid, and creasote can be readily distinguished from each other. The case, however, is very different when a mixture of the three substances has to be dealt with, as in the case of a sample of creasote adulterated with crude carbolic acid. As the problem is to detect the coal-tar acids in presence of wood-creasote rather than the reverse, only affirmative tests for the former bodies are of service, and in many cases these are seriously modified by the simultaneous presence of creasote. In fact, the glycerin and collodion tests are the only two of real service, and these are much affected by a considerable proportion of creasote. It is, however, possible to effect a partial separation of the substances by fractional distillation, so as to allow the tests for the coal-tar acids to be more readily applied. For this purpose the suspected sample is introduced into a small retort and distilled. The aqueous distillate is collected separately; the next portion (amounting to  $\frac{1}{5}$ th of the whole bulk of the liquid) is boiled to free it from water, and is then examined by glycerin and collodion in the manner already described. A considerably smaller proportion of the coal-tar acids can thus be detected than by operating on the original sample. The ferric chloride test is not of service for examining the distillate, as sufficient creasote is present to produce a brown coloration.

Fractional distillation also serves for the detection of alcohol, which is occasionally added to creasote.

According to Bouchard and Gimbert, none but pure wood-tar creasote ought to be used for internal administration, and a preparation intended for that purpose ought to stand the following tests:—It should boil at  $219^{\circ}$  C.; form a crystallisable salt with potash, but not with soda; produce no precipitate with collodion; and impart first a green and then a brown coloration to an aqueous solution of ferric chloride.

## ACID DERIVATIVES OF PHENOLS.

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By the action of oxidising agents, and in other manners direct and indirect, the phenols yield a great variety of acid derivatives. Many of these have received no applications at present in the arts or medicine, but a few are of considerable importance.

These will be considered in separate articles, together with a few other acids not directly derivable from, but closely related to, the phenols.

The chief acids derived from phenols which have received useful applications up to the present time, or which are otherwise important, are:—

SULPHOPHENIC ACID,  $\text{C}_6\text{H}_5\text{HSO}_4$ , obtained by the action of sulphuric acid on carbolic acid;

PICRIC ACID,  $\left. \begin{array}{c} \text{C}_6\text{H}_2(\text{NO}_2) \\ \text{H} \end{array} \right\} \text{O}$ , produced by the action of nitric acid on carbolic acid;

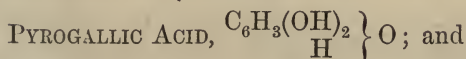
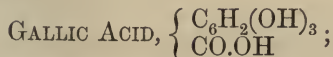
BENZOIC ACID,  $\left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CO.OH} \end{array} \right.$ , which has the constitution of phenyl-formic acid;

CINNAMIC ACID,  $\left\{ \begin{array}{c} \text{C}_9\text{H}_7\text{O} \\ \text{H} \end{array} \right\} \text{O}$ , or phenyl-acrylic acid;

SALICYLIC ACID,  $\left\{ \begin{array}{c} \text{C}_7\text{H}_5\text{O} \\ \text{H}_2 \end{array} \right\} \text{O}_2$ , which is one of three acids having the constitution of an oxybenzoic acid; and

PHTHALIC ACID,  $\text{C}_6\text{H}_4 \left\{ \begin{array}{c} \text{CO.OH} \\ \text{CO.OH} \end{array} \right.$ , the formula of which shows its relationship to benzoic and carbolic acids.

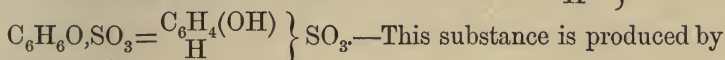
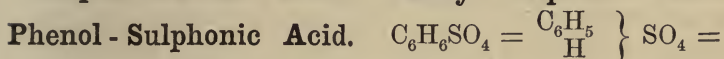
In addition to the above acids (and their derivatives) treated in this division—



CHRYSOPHANIC ACID,  $\text{C}_{15}\text{H}_{10}\text{O}_4$ , are distinctly related to the phenols, but have been already fully described in the division on vegetable acids.

## SULPHOPHENIC ACID.

**Sulpho-carbolic Acid. Phenyl-Sulphuric Acid.**



the direct action of concentrated sulphuric acid on carbolic acid. If the acids be diluted beyond a certain point no action takes place. Moderate heating and the presence of excess of sulphuric acid over the theoretical quantity are conditions facilitating the completeness of the reaction.\* Phenol is not miscible with sulphuric acid before combination, or much more soluble in dilute sulphuric acid than in water, but it is miscible in all proportions with concentrated sulphophenic acid, and in less than half its bulk of sulphophenic acid diluted with four volumes of water; addition of more water precipitates phenol, which is again dissolved on addition of sulphophenic acid. These facts are important, for they show that sulphophenic acid cannot be purified from carbolic acid by addition of water.

Phenyl-sulphuric acid is unknown in an absolute state. It is soluble in water and in alcohol, but insoluble in ether and chloroform. Its salts are all soluble in water, and mostly

\* Two distinct varieties of phenyl-sulphuric acid are said to be produced in this reaction, the *ortho*-acid being the chief product at the ordinary temperature, but being converted into the *para*-acid on heating.



soluble in alcohol, especially when hot, but are insoluble in ether. Carbohic acid in sulphophenic acid may be detected and separated by repeatedly shaking the liquid with ether free from alcohol. If the ether be spontaneously evaporated, the phenol may be detected by its odour, and by the yellow colour it develops when warmed with nitric acid and then saturated with potassa. A faint yellow tint must be neglected, owing to a trace of sulphophenic acid dissolving in the ether. Sulphophenic acid may also be purified from phenol by neutralising it with soda, and crystallising the resultant sulphophenate from alcohol.

The barium, calcium, and lead salts of sulphophenic acid are readily soluble. Hence sulphuric acid when present is readily detected and estimated by adding barium chloride.

Phenyl-sulphuric is a decided antiseptic, and its solutions coagulate albumin, but these properties are not shared by the sulphophenates until after addition of acetic acid. The free acid and its salts are said not to suffer decomposition in aqueous solution even when exposed to the air, and their solutions are but slowly decomposed by boiling.

A characteristic and delicate test for sulphophenic acid is to boil the liquid for a minute or two with an equal bulk of strong nitric acid, and then to neutralise the solution with potassa. A yellow colour, due to formation of potassium picrate, will be produced in a liquid containing 1 part of phenyl-sulphuric in 50,000 of water. Carbohic acid gives the same reaction. The reaction of sulphophenic acid with nitric acid also results in the formation of sulphuric acid. Hence, if any sulphates originally present be removed by the addition of excess of barium chloride, and the solution be then boiled with nitric acid, white insoluble barium sulphate will be thrown down if a sulphophenate were present,\* and from its weight the amount of sulphophenic acid may be calculated.

\* This reaction enables sulphophenic acid and sulphophenates to be readily detected in presence of carbohic acid.

( $C_6H_5HSO_4 : BaSO_4 :: 173 : 233$ .) The yellow liquid contains picric acid.

Another delicate test for phenyl-sulphuric acid is the production of a deep purple colour with ferric chloride. The colour is discharged by acids.

Several of the sulphophenates, notably the calcium and sodium salts, have been employed in medicine as a means of internally administering carbolic acid.

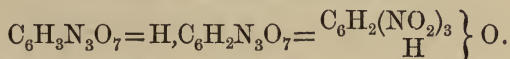
**Sulpho-cresylic Acid.** Cresyl-sulphuric Acid.  $C_7H_8SO_4 = \left. \begin{matrix} C_7H_7 \\ H \end{matrix} \right\} SO_4$ .—This acid is produced by the action of sulphuric acid on cresol, and closely resembles its lower homologue. Para-cresyl-sulphuric acid exists as a potassium salt in the urine of horses, and probably of other mammals. Baumann has shown that if the sulphates be first precipitated by acidulating the urine with acetic acid and warming the diluted liquid with excess of barium chloride, the filtered liquid will contain any cresyl-sulphates and phenyl-sulphates which may be present. On warming the filtrate for one hour with hydrochloric acid these are decomposed, barium sulphate being precipitated, together with resinous matter from which it may be freed by washing with hot alcohol.

## PICRIC ACID.

### Tri-nitro-phenic Acid. Carbazotic Acid.

*French*—Acide Pierique.

*German*—Kohlenstickstoff-säure.



The substance is a frequent product of the action of nitric acid on organic bodies. Thus, it is obtainable from indigo, aloes, gum-resins, wool, silk, &c. In practice, it is now almost always made by dissolving crystallised carbolic acid in strong sulphuric acid, and adding either nitric acid or sodium nitrate to the resultant sulphophenic acid. Mono- or di-nitrophenic acid may result if the action be not carried sufficiently

far. The crude acid is purified by exact neutralisation with sodium carbonate, with filtration to separate resin, and a large excess of sodium carbonate added to the filtrate, when sodium picrate is precipitated. This salt is decomposed by sulphuric acid, and the picric acid crystallised.

Picric acid occurs in pale yellow crystalline needles or scales, of an intensely bitter taste. The pure acid melts at  $122^{\circ}\text{C}$ ., and the common at  $114^{\circ}$  to  $115^{\circ}\text{C}$ ., to a brownish yellow oil, which at a higher temperature partially sublimes, and boils with formation of yellow, bitter, suffocating vapours. The lower melting point of impure picric acid is probably due to an admixture of di-nitro-phenic acid, which melts at  $104^{\circ}\text{C}$ . Hence, the melting point of picric acid is a test of its purity.

Picric acid is pretty readily soluble in boiling water, but it requires nearly 100 parts at  $15^{\circ}\text{C}$ . The solution is intensely bitter, bright yellow, and reddens litmus. In a stratum of 1 inch in depth, the yellow colour of a solution of 1 part of picric acid in 30,000 of water is distinctly visible. The yellow colour of picric acid solutions is intensified by neutralisation with an alkali.

Picric acid is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, &c.; the last two solutions are colourless. Such of the above solvents as are not miscible with water remove picric acid from an aqueous solution which has been freely acidulated with sulphuric acid. In the absence of sulphuric acid, the removal of the picric acid is very incomplete.

All the above solutions of picric acid, including the aqueous, dye silk, wool, skin, and other nitrogenous organic matter a bright yellow colour. The stain is not removeable by water, but soap or alkali partly destroys it.

Picric acid is liable to explode when strongly heated. This property is more marked in some of its salts, which have been employed in several detonating and explosive mixtures.

When a solution of picric acid is boiled with a strong solu-

tion of potassium cyanide, a deep red liquid is produced, owing to the formation of potassium iso-purpurate, which crystallises in small reddish-brown plates with a beetle-green lustre. This, by reaction with ammonium chloride, gives ammonium iso-purpurate,  $\text{NH}_4\text{C}_8\text{H}_4\text{N}_5\text{O}_6$ , or artificial murexide, which dyes silk and wool a beautiful red colour. On adding barium chloride to a solution of either of the above salts a vermilion-red precipitate is formed, consisting of barium iso-purpurate.

Solution of picric acid gives a bright green precipitate on addition of ammonio-sulphate of copper.

Picric acid, when boiled with a strong solution of calcium hypochlorite (bleaching powder), gives off pungent and tear-exciting vapours of chloropicrin,  $\text{CNO}_2\text{Cl}_3$ .

Picric acid may be determined by extracting the acidulated aqueous solution by agitation with ether or benzene, and subsequently removing and evaporating off the solvent. It may also be precipitated as a potassium or cinchonine salt (see page 330).

**Detection of Picric Acid in Beer.**—Picric acid has been frequently used to communicate a bitter taste to beer. Its employment in this manner as a "hop-substitute" is objectionable on several grounds. The following method may be employed for its detection:—Acidulate the beer with hydrochloric acid, immerse a small quantity of white Berlin wool in the liquid, and heat it on the water-bath for some time. In presence of picric acid the wool acquires a yellow colour. If this be rendered indistinct by the colouring matter of the beer, the dye may be removed from the wool by warming it with dilute ammonia, filtering; and evaporating the filtrate on the water-bath to a very small bulk. On adding a few drops of cyanide of potassium solution and heating, a distinct red colour will be produced in presence of picric acid.

A more delicate and satisfactory method is to concentrate



100 c.c. of the beer by evaporation to about 30 c.c.; then acidulate with sulphuric acid, and agitate with ether or petroleum spirit. The upper layer of liquid is drawn off, allowed to evaporate spontaneously, and the residue dissolved in water. The aqueous liquid is heated with white wool, which in presence of picric acid will acquire a yellow colour. The author has readily detected 1 part of picric acid in 100,000 of beer by the above method. Amylic alcohol has been proposed as a substitute for ether, but is not so satisfactory. H. C. Sorby examines the yellow aqueous liquid obtained as above in the *micro-spectroscope*, instead of boiling wool in it. Picric acid absorbs the blue end of the spectrum, but on addition of dilute sulphuric acid the absorption almost wholly disappears. The effect on the spectrum should be compared with that produced by a beer of known purity.

**Commercial Picric Acid** is liable to contain various impurities, and is occasionally intentionally adulterated. The following methods serve for its assay:—

RESINOUS AND TARRY MATTERS are not unfrequently present. They are left insoluble on dissolving the sample in boiling water. The separation is more perfect if the hot solution be exactly neutralised by caustic soda.

SULPHURIC, HYDROCHLORIC, AND OXALIC ACIDS, and their salts are detected by adding to the filtered aqueous solution of the sample, solutions of the picrates of barium, silver, and calcium. These salts are readily made by boiling picric acid with the carbonates of the respective metals and filtering; other soluble salts of these metals may be substituted for the picrates, but they are less satisfactory.

NITRIC ACID may be detected by the red fumes evolved on warming the sample with copper turnings.

INORGANIC IMPURITIES and picrates of potassium and sodium, &c., leave residues on cautious ignition.

GENERAL IMPURITIES AND ADULTERATIONS may be detected and determined by shaking 1 gramme of the sample of acid in

a graduated tube with 25 c.c. of ether. The pure acid dissolves, while any oxalic acid, nitrates, picrates, boric acid, alum, sugar, &c., will be left insoluble, and after removal of the ethereal liquid, may be readily identified and determined. For the detection and determination of water and of oxalic acid, 50 c.c. of warm benzene may be advantageously substituted for the ether. Sugar may be separated from the other impurities by treating the residue insoluble in ether or benzene with rectified spirit, in which sugar and boric acid alone will dissolve. If boric acid be present, the alcoholic solution will burn with a green flame.

MONO- AND DI-NITROPHENIC ACIDS lower the melting point of the sample (see page 327). Their calcium salts are less soluble than the picrate, and may be approximately separated from it by fractional crystallisation, or by precipitating the hot saturated solution of the sample with excess of lime water.

**Potassium Picrate.**— $K, C_6H_2(NO_2)_3O$ .—When a strong solution of picric acid is neutralised by carbonate or hydrate of potassium, this salt is thrown down in yellow crystalline needles. Potassium picrate requires 260 parts of cold or 14 parts of boiling water for solution; in alcohol it is much less soluble. The aqueous solution of potassium picrate is much more strongly coloured than a solution of free picric acid of corresponding strength. Picric acid may be approximately determined by precipitation as potassium picrate.

Ammonium Picrate is more soluble than the potassium salt, and sodium picrate is readily soluble in pure water, but nearly insoluble in solution of carbonate of sodium. (See page 337.)

**Picrates of Alkaloids.**—Picric acid forms insoluble salts with many of the alkaloids. Thus, the cinchona alkaloids, the opium alkaloids (except morphia and pseudo-morphia), the *strychnos* alkaloids, veratria, and some others are completely

precipitated from their dilute solutions if acidulated with sulphuric acid; not with hydrochloric acid. Caffeine and the glucosides are not precipitated by picric acid. Owing to the insolubility of picrate of cinchonine, picric acid may be determined in the following manner. To the solution of picric acid or a picrate, add a solution of sulphate of chinchonine acidulated with sulphuric acid. The precipitate of picrate of cinchonine,  $C_{20}H_{24}N_2O(C_6H_2N_3O_7)_2$ , is washed with cold water, rinsed off the filter into a porcelain crucible or dish, the water evaporated on the water-bath, and the residual salt weighed. Its weight, multiplied by .6123, gives the quantity of picric acid in the sample taken.

**Picrates of Hydrocarbons.**—Picric acid when added to certain hydrocarbons in alcoholic solution, combines with them to form characteristic crystalline compounds. This reaction has been utilised for the purpose of distinguishing hydrocarbons, especially those of the naphthalene series. The subject will be further referred to in the section treating of these hydrocarbons.

**Bodies analogous to Picric Acid.**—When cresylic acid, is acted on by nitric acid, it produces a series of nitro-compounds closely resembling the mono-, di-, and tri-nitrophenic acids. Thus sodium di-nitro-cresylate,  $C_7H_5Na(NO_2)_2O$ , is known in the arts as "Victoria-yellow." The potassium salt forms red crystals known as "gold-yellow."

"Manchester-yellow" or "naphthalene-yellow" consists of the sodium or calcium salt of di-nitro-naphthalic acid,  $C_{10}H_6(NO_2)_2O$ , produced by the action of nitric acid on naphthol, a phenol-like body obtained from naphthalene. Naphthalene-yellow dyes wool and silk a brilliant yellow colour, free from the greenish reflection peculiar to fabrics dyed with picric acid. The two dyes may be distinguished by boiling wool in the acidified solution, washing it, heating it with ammonio-sulphate of copper, and again washing. When a fibre or fabric dyed with picric acid is thus

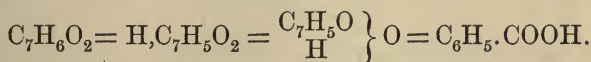
treated, it turns bluish-green, but if naphthalene-yellow was used, an olive-green tint results.

Either of the above dyes may be extracted from a fabric by hot dilute ammonia, which dissolves them with yellow colour. Aurin or rosolic acid forms a magenta-red liquid when similarly treated, and also on warming with lime water or dilute soda.

## BENZOIC ACID.

*French*—Acide Benzoïque.

*German*—Benzosäure.



Benzoic acid occurs ready formed in gum benzoin, storax, Tolu and Peruvian balsams, &c., and is produced by the oxidation of a great variety of organic bodies, including benzoic and cinnamic aldehydes, toluene, cumene, casein, gelatin, &c. In practice it is obtained from one of the three following sources:—

1. GUM BENZOIN. This is a resinous substance which exudes from the bark of *Styrax benzoin*, a tree growing in the Malay Archipelago. The gum usually contains about 12 or 14 per cent. of benzoic acid, which may be extracted by sublimation or by exhaustion of the powdered gum with carbon disulphide.

2. COW'S or HORSE'S URINE contains a body known as hippuric acid,  $\text{C}_9\text{H}_9\text{NO}_3$ , which on putrefaction of the urine splits up into benzoic acid and glycocine ( $\text{C}_9\text{H}_9\text{NO}_3 + \text{H}_2\text{O} = \text{C}_7\text{H}_6\text{O}_2 + \text{C}_2\text{H}_5\text{NO}_2$ .) Benzoic acid is obtained on a large scale by treating putrid cow's urine with lime, filtering, concentrating the filtrate, and precipitating the benzoic acid with excess of hydrochloric acid. Benzoic acid prepared in this way is apt to retain a smell of urine.

3. PHTHALIC ACID, obtained by acting on naphthalene  $\text{C}_{10}\text{H}_8$ , by nitric acid, when heated with excess of slaked lime, yields a mixture of calcium carbonate and benzoate



( $C_8H_6O_4 = CO_2 + C_7H_6O_2$ ), from which benzoic acid may be readily prepared. An acid prepared in this way always smells of oil of bitter-almonds.

Benzoic acid is a white solid occurring in crystalline lustrous scales or friable needles. When pure it is nearly odourless, but it generally smells of benzoin, and sometimes of urine. The odour is an indication of its origin. Benzoic acid requires 200 parts of cold or 12 of boiling water for solution. Its solubility is greatly increased by the presence of certain salts, notably sodium phosphate. Benzoic acid is readily soluble in alcohol, ether, chloroform, carbon disulphide, benzene, and petroleum spirit. Benzoic acid fuses at  $120^\circ C.$ , and sublimes without decomposition at a higher temperature; it may thus be separated from fixed impurities.

Distilled with excess of lime, benzoic acid yields benzene,  $C_6H_6$ .

When benzoic acid is dissolved or suspended in warm water acidulated with a drop or two of dilute sulphuric acid, and a strip of magnesium ribbon is added, hydride of benzoyl, ( $C_7H_5O.H$ ), is formed, having a smell of bitter-almond oil. The same substance results when benzoic acid vapours are passed over faintly ignited zinc-dust.

Free benzoic acid possesses decided antiseptic properties, being, according to some observers, superior in this respect to salicylic acid. Four grains of benzoic acid added to each pound of preserves will effectually prevent fermentation.

DETECTION AND DETERMINATION OF BENZOIC ACID.—The Benzoates are mostly soluble in water. Their strong solutions are precipitated on addition of hydrochloric acid, owing to the slight solubility of benzoic acid in water. Succinates give no precipitate with hydrochloric acid. Hippurates and cinnamates react like benzoates. Sulphuric acid should not be substituted for the hydrochloric. The separated benzoic acid dissolves on agitation with ether, chloroform, or benzene. (Hippuric acid is not dissolved.)

Ferric chloride previously treated with as much dilute ammonia as can be added without the formation of a permanent precipitate, precipitates neutral benzoates almost completely as a light-red bulky basic ferric benzoate, insoluble in acetic acid. Succinates give a similar reaction, but cinnamates give a yellow precipitate, and salicylates a purple coloration. Benzoic acid is also distinguished from succinic and many other acids by not being precipitated by ammoniacal chloride of barium in presence of alcohol. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

Benzoic acid may be separated from fixed substances by sublimation. It may be determined in gum benzoin by the following method:—the sample is powdered, mixed with sand, and the mixture heated in a beaker or earthenware jar, furnished with a cap of filter-paper pierced with small holes. Over this is placed a cone or hood of stout paper. The benzoic acid sublimes and condenses on the inside of the hood, any oil and impurities being retained by the diaphragm of filter-paper.

Another method for the approximate assay of gum benzoin is to digest 10 parts of the powdered gum with 6 parts of slaked lime, and 100 parts of water. After six hours, the liquid is boiled, filtered, and the residue washed. The filtrate is concentrated, rendered strongly acid with hydrochloric acid, and thoroughly cooled. The precipitated benzoic acid is filtered off, washed with a little cold water, and dried between folds of blotting-paper. The small quantity of acid retained in the mother liquor may be extracted by agitation with chloroform, and the residue left by the spontaneous evaporation of the chloroform may be added to the main quantity of benzoic acid. A preferable plan is to agitate the acidulated liquid at once with chloroform, without filtering off the precipitated benzoic acid, and to subsequently recover the benzoic acid from its chloroformic solution by the spontaneous evaporation of the solvent, assisted by a current of dry air from a bellows. If

ether be substituted for the chloroform the product contains a smaller quantity of water, and the determination is too high.

Benzoic acid may also be approximately estimated, in the absence of interfering substances, by converting it into a soluble neutral benzoate, and precipitating the solution with lead acetate. The benzoate of lead is filtered off, washed once with cold water, then with proof-spirit containing  $\frac{1}{2}$  per cent. of acetic acid, and finally dried at  $100^{\circ}$  C. and weighed. The weight found, multiplied by .5434, gives the amount of benzoic acid present.

**Commercial Benzoic Acid** is liable to contain various impurities, some of which are due to its mode of preparation, while others are intentionally added as adulterants. Asbestos, calcium carbonate and sulphate, sal-ammoniac and sugar belong to the latter class. On treating a sample of benzoic acid with ether, nearly all impurities and adulterates, except cinnamic acid and essential oil, are left undissolved.

**FIXED IMPURITIES** in benzoic acid can be detected and estimated by subliming the sample, pure benzoic acid being readily and entirely volatile. If the residue chars on further heating, sugar or hippuric acid may be present. The former gives a smell resembling burnt bread, and the latter a odour of burnt feathers. Of course sugar and hippuric acid are readily distinguished in other ways, such as their very different solubility in cold water.

**INORGANIC IMPURITIES**, such as chalk, gypsum, or asbestos, if present, will be left as a residue on igniting the sample of benzoic acid. The first dissolves readily with effervescence in dilute hydrochloric acid. The second dissolves with difficulty, and the solution gives a white precipitate with barium chloride. Asbestos, clay, &c., are insoluble in dilute hydrochloric acid.

**HIPPURIC ACID**, when present, may be detected by the be-

haviour of the sample on heating; by its incomplete solubility in ether; by its charring when heated with strong sulphuric acid; and by the evolution of ammonia which occurs when the sample is ignited with soda-lime. The last reaction may be employed quantitatively in the absence of ammoniacal salts. The proportion of hippuric acid may be approximately determined by agitating the sample with dilute hydrochloric acid and benzene or chloroform, when the benzoic acid dissolves, but any hippuric (or succinic) acid remains.

Samples of benzoic acid containing hippuric acid usually have a urinous odour, and redden or char when heated.

CINNAMIC ACID is best detected by its reaction with manganous salts (see page 338), and by the smell of bitter-almond oil produced on warming the sample with sulphuric acid and potassium bichromate.

SUGAR is recognised by its insolubility in ether, ready solubility in cold water, and by the blackening which occurs when the sample is heated with strong sulphuric acid. When present in quantity it may be detected by the taste of the sample, and in smaller quantity by the taste of the residue left undissolved by ether or chloroform.

SAL-AMMONIAC is readily detected by shaking the sample with cold water, when a solution is obtained which on addition of argentic nitrate gives white curdy chloride of silver, insoluble in nitric acid. This proves the presence of a chloride only; the presumption that sal-ammoniac is present is confirmed if the sample evolves ammonia on treatment *in the cold* with caustic alkali. In presence of sal-ammoniac and other ammoniacal salts, the soda-lime test for hippuric acid is inapplicable, unless the sample be first shaken with cold moderately concentrated hydrochloric acid, in which ammonium chloride dissolves, while hippuric acid is nearly insoluble.

ESSENTIAL OIL, which is very commonly present in the acid made from gum-benzoin, causes the sample to turn brown



when warmed with strong sulphuric acid. Resinous and oily matters may also be detected by dissolving the sample in warm solution of soda, in quantity just sufficient for its neutralisation, when such impurities will remain undissolved, together with any asbestos, chalk, &c.

Traces of sulphuric and hydrochloric acid are frequently present in benzoic acid, owing to the mode of preparation.

**Cinnamic Acid**,  $C_9H_8O_2 = C_9H_7O.OH$ .—This acid occurs readily formed in Tolu and Peruvian balsam, and in some samples of gum benzoin; also in old oil of cinnamon. It closely resembles benzoic acid, but strong solutions of its salts give a yellow precipitate with ferric chloride, and a white precipitate with manganous sulphate or chloride (avoiding an excess of the precipitant). Benzoates are not precipitated by manganous salts.

Cinnamic acid is also distinguished by its behaviour when heated with sulphuric acid and potassium bichromate. Cinnamic acid and cinnamates reduce the chromate, with production of a green colour and an odour of bitter-almond oil. Benzoic acid gives a negative result when similarly treated.

The following table, due to Kachler,\* shows the melting points of various mixtures of cinnamic and benzoic acids:—

Cinnamic Acid. Per Cent.	Benzoic Acid. Per Cent.	Melting Point. °C.
100	0	133·3
99	1	131·8
90	10	126·6
80	20	118·0
70	30	108·2
60	40	98·7
50	50	84·3
40	60	87·1
30	70	101·4
20	80	106·4
10	90	111·5
1	99	118·2
0	100	123·3

\* *Zeitsch. f. Chem.* vi. 59.

CINNAMIC ALDEHYDE,  $C_9H_8O$ , is the essential constituent of the oils of cinnamon and cassia. It yields cinnamic acid by the action of air, and benzoic aldehyde and acid by treatment with nitric acid.

**Benzoic Aldehyde**; Hydride of Benzoyl; Essential Oil of Bitter-almonds; Peach-nut Oil.

*French*—Huile d'amandes amères.



Pure benzoic aldehyde is a thin colourless liquid of great refractive power and peculiar, very agreeable odour. Its density is 1.043, and its boiling point  $180^\circ C$ . It is soluble in about 300 parts of water,\* and is miscible in all proportions with alcohol and ether.

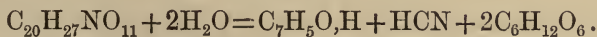
Exposed to the air, benzoic aldehyde absorbs oxygen greedily, and is converted into a crystalline mass of benzoic acid. Heated with solid caustic alkali, benzoyl hydride evolves hydrogen, and yields a benzoate.

Like all true aldehydes, hydride of benzoyl forms crystalline compounds with the acid sulphites of the alkali-metals. The sodium compound has the formula  $C_7H_5NaSO_3$ .

Benzoic aldehyde burns when ignited with a luminous smoky flame.

Pure benzoic aldehyde is not poisonous.

CRUDE NATURAL ESSENTIAL OIL OF BITTER-ALMONDS results from the maceration of bitter-almonds with water, with subsequent distillation. Both sweet- and bitter-almonds contain a nitrogenised body called amygdalin, which under the influence of a ferment called synaptase, present in the bitter-almond only, is split up into hydride of benzoyl, hydrocyanic acid, and glucose.



From 160 to 200 parts of bitter-almonds are required for

\* The solubility is often erroneously stated at 1 in 30, or ten times the true amount.

the production of 1 part of the oil. Crude natural oil of bitter-almonds has a density varying from 1.04 to 1.075 (never more), and contains, in addition to benzoic aldehyde, benzoic and hydrocyanic acids, benzoïn, ( $C_{14}H_{12}O_2$ ), and benzimide. By fractional distillation, hydrocyanic acid passes over first, and then tolerably pure hydride of benzoyl. Benzoïn is a solid camphor-like body, and occurs most largely in samples of oil of high density, in the preparation or purification of which a high temperature has been employed. It gives a purple colour with strong sulphuric acid. Bitter-almond oil gives a crimson coloration with strong sulphuric acid, becoming brownish on exposure to the air. If the crimson liquid be poured into water the red colour disappears, and a yellow precipitate is produced, which sometimes takes the form of globules. The usual proportion of hydrocyanic acid in crude almond oil is about 8 per cent., but it sometimes reaches twice this amount. Of course the presence of hydrocyanic acid renders the oil poisonous; indeed, it is from four to eight times as strong in hydrocyanic acid as the "B. P." acid. When present, hydrocyanic acid may be detected in bitter-almond oil by agitating the sample with water, and applying the tests for hydrocyanic acid to the aqueous liquid. Ferric chloride and ferrous chloride or sulphate should be added, and then solution of soda. On acidulating the liquid with hydrochloric acid, a bluish-green coloration or prussian-blue precipitate will be formed, if hydrocyanic acid be present. An aliquot part of the aqueous solution may be employed for the determination of the hydrocyanic acid by precipitation or titration with nitrate of silver (see page 32). Hydrocyanic acid may be removed from bitter-almond oil by agitating the sample with mercuric oxide and water, or with lime and ferrous chloride, followed in either case by distillation of the oily layer.

**BITTER-ALMOND WATER** is a pharmaceutical preparation consisting of a solution of bitter-almond oil in water. Its

strength is very uncertain, however closely the specified directions are adhered to. It always contains hydrocyanic acid, the proportion varying from  $\frac{1}{4}$  to 1 per cent. The quantity may be determined by titration with standard nitrate of silver, as described on page 34. Laurel water (*Aqua lauro-cerasi*), prepared by distilling laurel leaves, and cherry water, from wild cherries, are very similar preparations to bitter-almond water. Bitter-almond water becomes milky immediately on addition of ammonia, an effect not produced on laurel water till after the lapse of some time.

ARTIFICIAL HYDRIDE OF BENZOYL is prepared by the action of chlorine on hot toluene,  $C_7H_8$ , by which chloride of benzyl,  $C_7H_7Cl$ , results, and this yields the benzoic aldehyde on distillation with nitrate of lead and water in an atmosphere of carbonic acid. The product is purified by conversion into the acid sulphite compound. Artificial hydride of benzoyl is free from hydrocyanic acid, but is liable to retain traces of chlorine or bromine compounds. These may be detected by passing the vapour, together with hydrogen, through a red-hot tube, as described under "chloroform" (page 175).

ESSENCE OF BITTER-ALMONDS is the name given to a solution of 1 part of the commercial oil of bitter-almonds in 3 of rectified spirit. It is employed as a flavouring agent, for which purpose it should be quite free from hydrocyanic acid. "Almond flavour" is a solution of 1 part of the oil in 7 of rectified spirit. Oil of bitter-almonds is frequently adulterated by an unacknowledged addition of alcohol. When the proportion of the adulterant reaches 8 or 10 per cent. it may be detected by mixing the sample with an equal measure of fuming nitric acid, which in presence of alcohol causes, on warming, brisk effervescence, with formation of red fumes. Addition of alcohol reduces the density of oil of bitter-almonds. The proportion of alcohol present as an adulterant in the oil of bitter-almonds may be approximately



ascertained by shaking the sample in a graduated tube with an equal measure of water or glycerin, and noting the reduction in volume of the oily layer. With a larger proportion of alcohol, such as is present in the essence, this method fails, and the alcohol is best separated by fractional distillation.

ARTIFICIAL ESSENCE OF BITTER-ALMONDS is a name frequently given to nitrobenzene,  $C_6H_5NO_2$ , which is also much used to adulterate the genuine oil. Nitrobenzene has a density of 1.186, and hence is heavier than bitter-almond oil. It also differs from hydride of benzoyl in not yielding benzoic acid when a current of air is passed through it. The following method may be employed for the detection and approximate estimation of nitrobenzene in bitter-almond oil:—

Introduce some clean sand or emery into a wide-mouthed flask, and then add a known weight (about 10 grammes) of the sample to be tested; next add 40 c.c. of a saturated aqueous solution of acid sulphite of sodium ( $NaHSO_3$ ), agitate briskly for a few minutes, and then shake with ether free from alcohol. The benzoic aldehyde forms a compound with the sulphite, while any nitrobenzene dissolves in the ether. The upper layer is withdrawn by a pipette, more ether added, and the agitation repeated. The pipette being again used, the united ethereal liquids are evaporated by a gentle heat, and the residual nitrobenzene is weighed. The method is only roughly approximate. If the quantity of nitrobenzene be small, or there be any doubt as to its identity, four or five drops should be dissolved in alcohol, and heated for some time with hydrochloric acid and granulated zinc. The nascent hydrogen reduces the nitrobenzene to aniline,  $C_6H_7N$ . The liquid is filtered through wet paper, rendered alkaline with solution of soda,\* agitated with ether, the ethereal layer removed, evaporated, and the residual aniline treated with a

\* When the nitrobenzene occurs in quantity, bleaching-powder may be added at once to the filtered liquid, after nearly neutralising it with soda.

drop or two of dilute sulphuric acid and shaken with water. A dilute solution of bleaching-powder is cautiously added to the aqueous liquid, when, if nitrobenzene were originally present, a violet colour (mauve) will be developed. The process requires to be skilfully conducted. This method may be conveniently used for distinguishing bitter-almond oil from nitrobenzene, but not for detecting the latter in presence of the former; when this is required, the sulphite and ether process must be previously used for their separation.\*

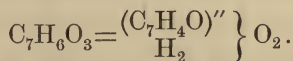
The following method for detecting and approximately determining nitrobenzene in bitter-almond oil is due to Maisch:†—

Dissolve 1 c.c. of the sample in 12 c.c. of absolute alcohol, and add  $\frac{3}{4}$  gramme of fused caustic potash. Boil the liquid till it is reduced to about 4 c.c., and leave it to cool. If the sample be pure no crystals form, but a brown colour is slowly developed. The residual liquid is entirely soluble in water. In presence of nitrobenzene, brown crystals of a z-oxybenzene,  $(C_{12}H_{10}N_2O)$ , are formed, which are insoluble in water, and may be collected, dried by pressure, and weighed.

## SALICYLIC ACID.

### Meta-oxybenzoic Acid.

*French*—Acide Salicylique.



This substance was originally prepared from salicin,  $C_{13}H_{18}O_7$ , a bitter principle existing in willow bark. It has since been obtained from other sources, and is now prepared on a considerable scale by a process of which the following is an outline:—

Crude soda-lye of known strength is exactly saturated by

\* Most other essential oils can also be separated from hydride of benzoyl by means of acid sodium sulphite and ether.

† I have no experience of this process. For other methods, see *Year-Book of Pharmacy*, 1872, p. 44.

crystallised carbolic acid, and the liquid cautiously evaporated till the residue is perfectly dry. It is then subjected to the action of a stream of carbonic acid gas at a temperature commencing at  $100^{\circ}$  C., which is gradually raised to  $180^{\circ}$ , and may reach  $220^{\circ}$  to  $250^{\circ}$  C. towards the close of the operation. During this process, carbolic acid distils over and ultimately amounts to half the quantity taken. The residue in the retort is basic sodium salicylate, the solution of which on treatment with hydrochloric acid yields a precipitate of impure brown salicylic acid. This is washed and distilled at  $170^{\circ}$  C. in a current of superheated steam, when it is obtained perfectly white. If carbolic acid containing cresylic acid be used, the salicylic acid contains cresotic acid (see page 347), which possesses many of the properties of salicylic acid; but for internal medicinal use pure salicylic acid should be employed. Salicylic acid usually occurs as a granular powder, consisting of minute broken acicular crystals, which are rarely quite colourless. It melts at  $125^{\circ}$  C.,\* and sublimes at about  $200^{\circ}$  C. in slender shining needles.† Salicylic acid is nearly insoluble in cold water, but readily dissolves in hot; on cooling, the acid is deposited, about 1 part in 300 remaining in solution. Salicylic acid is a powerful antiseptic; and, owing to its slight taste, is employed for preserving beer, milk, lime- and lemon-juice, gum, and other fluids. By the presence of various neutral salts, its solubility is increased without its antiseptic value being interfered with. Thus—

Mixed with 1 part potassium nitrate, it dissolves in 50 parts cold water.

„	$1\frac{1}{2}$ part ammonium citrate,	„	60	„
„	2 parts sodium sulphite,	„	50	„
„	2 parts sodium phosphate,	„	50	„
„	$2\frac{1}{2}$ parts sodium phosphate,	„	$12\frac{1}{2}$	„

\* The high melting point of some commercial samples of salicylic acid is probably due to an admixture of cresotic acid.

† Sublimed salicylic acid is liable to contain carbolic acid. Salicylic acid evaporates largely with vapour of water on boiling the solution. The presence of foreign matters in solutions of salicylic acid greatly interferes with its crystallisation, so that the facile formation of definite crystals is a test of its purity.

Salicylic acid is very soluble in solutions of borax, but the liquid soon undergoes decomposition. A compound of the formula  $\text{Na}(\text{BO})_2\text{C}_7\text{H}_5\text{O}_3$  is said to be formed by the reaction of borax and salicylic acid.

Salicylic acid is readily soluble in alcohol and ether. Agitation with ether removes free salicylic acid from its aqueous solutions.

The distillation of salicylic acid with excess of lime produces calcium carbonate and phenol.

Concentrated sulphuric acid dissolves pure salicylic acid without colour, forming a sulpho-acid. Impure salicylic acid gives a yellowish brown coloration.

On distilling salicylic acid or one of its salts with wood-spirit and sulphuric acid, acid methyl salicylate is condensed, having an agreeable aromatic odour. (See page 144.)

Nitric acid forms nitro-salicylic acid; with fuming nitric acid, picric acid results.

Argentie nitrate and lead acetate give white precipitates with neutral salicylates, but not with free salicylic acid.

Bromine gives the same reaction with salicylic acid as with phenol, and the same is true of Millon's reagent (see page 307).

The most delicate reaction for salicylic acid is that with ferric chloride, which produces a beautiful violet colour even in extremely dilute solutions. The colour is destroyed by acids and by alkalies. The reaction is greatly more delicate (1 in 100,000) than that of phenol with the same reagent (1 in 3000).

Weiske proposes to employ the above reaction in alkali-metry. On neutralising an acid solution to which a trace of salicylic acid and ferric chloride have been added, the violet colour becomes gradually more developed until neutrality is reached, when the liquid turns reddish-yellow.

Dr Muter has utilised the reaction with ferric chloride for the volumetric assay and determination of salicylic acid. Some very pure acid is first obtained by the recrystallisation and



dialysis of the commercial substance, and of the pure crystals thus obtained 1 gramme is dissolved in a litre of water. The indicator is a very weak solution of pure neutral ferric chloride, of such a strength that 1 c.c. added drop by drop to 50 c.c. of the standard acid ceases to give any increase in intensity of colour just before the addition of the last drop or two. One gramme of the sample of salicylic acid is dissolved in 1 litre of water and 50 c.c. placed in a Nessler cylinder, 1 c.c. of the ferric solution added, and the colour observed after standing five minutes. Its depth is compared with that of the standard solution, diluted as thought necessary, and treated in a similar way. In presence of small quantities of free acetic acid, ten minutes should be allowed instead of five. Mineral acids must be absent. Neutral mineral salts have no action, provided they do not affect the iron-salt. Casein and certain albuminous bodies interfere; and hence, for the detection of salicylic acid in milk,\* Dr Muter proceeds as follows:—

Four ounces of the sample are dialysed for twelve hours on a pint of distilled water, when half an ounce of the dialysed liquid is taken, placed in a narrow tube, and a little of the ferric chloride solution added, the tint being observed over white paper. If no violet colour be produced, the milk is pure; but otherwise the dialysis is continued for forty-eight hours. For estimation of the total quantity, an equal volume of pure milk should be dialysed, so as to give a comparison liquid to be used instead of water for the dilution of the standard solution. The process is then proceeded with as detailed in the last paragraph. The method may be modified by rendering the dialysed liquid slightly alkaline with soda, concentrating it by evaporation, acidifying with hydrochloric acid, and shaking the liquid with ether, which dissolves the salicylic acid.

The results by the dialysis process are about 90 per cent. of the true amount present. The same method may be used for examining beer.

\* *Analyst*, i. 194.

For the detection of salicylic acid in wine or urine, M. E. Robinet takes 100 c.c. of the sample, precipitates with excess of lead acetate, adds sulphuric acid to the filtrate as long as a precipitate is produced, again filters, and tests the liquid with ferric chloride. Care should be taken to neutralise the liquid before adding ferric chloride. By proceeding as described by Dr Muter, this method might readily be made quantitative.

COMMERCIAL SALICYLIC ACID is often very impure. Chloride of sodium, carbolic acid, cresotic acid, and oxybenzoic and para-oxybenzoic acids are the usual impurities. The first of these substances remains on igniting the acid. Carbolic acid may be detected by nearly neutralising the sample with soda and agitating the liquid with ether. On evaporation, the ethereal liquid leaves the carbolic acid recognisable by its smell and taste.

Muter gives the following test for carbolic acid in samples of salicylic acid:—Boil 10 grains in half an ounce of water, cool, decant the solution, and add to it 1 minim of a saturated solution of bicarbonate of potassium, ( $\text{KHCO}_3$ ), 1 minim of aniline, and 5 drops of solution of bleaching powder, when, if carbolic acid be present, a deep blue colour will be produced.

A mode of recognising cresotic acid in samples of salicylic acid is given on the next page, and tests for distinguishing salicylic from the other oxybenzoic acids on page 349.

H. Kolbe gives the following method of testing the purity of salicylic acid:—

Dissolve  $\frac{1}{2}$  gramme of the sample in 5 or 6 c.c. of strong alcohol, pour the clear solution into a watch-glass, and allow it to evaporate spontaneously. The residual salicylic acid forms a ring round the edge of the watch-glass of beautifully aggregated efflorescent crystals. This mass is pure white if the acid tested be pure and recrystallised, but yellowish or yellow if the simply precipitated acid be used. If the colour be brownish or brown, the sample is unfit for internal use.

**Cresotic Acid**,  $\text{C}_8\text{H}_8\text{O}_3$ .—This homologue of salicylic acid

is prepared from cresylic acid in a similar manner to that used for obtaining salicylic from carbolic acid. It closely resembles salicylic acid. Two isomeric modifications are obtainable from coal-tar cresol, one melting at  $173^{\circ}$  C., and the other at  $115^{\circ}$  to  $120^{\circ}$  C. The formation of these products confirms the presence of two varieties of cresol in coal-tar. Other modifications of cresotic acid appear to exist.

The properties of commercial artificial salicylic acid are often much modified by the presence of cresotic acid. Thus, pure salicylic acid requires about 22 parts of boiling water for solution, while samples containing cresotic acid dissolve in 14 of boiling water, or even in a smaller proportion. If to the solution so obtained about  $\frac{1}{4}$ th of alcohol be added, and the liquid allowed to cool, pure salicylic acid will form separate distinct crystals not cohering together, while samples containing cresotic acid form a network or woolly mass of small or indistinct crystals.

If to the boiling aqueous solution of impure salicylic acid excess of carbonate of calcium be added, and the liquid be filtered while hot, sparingly soluble salicylate of calcium is deposited as the solution cools. When re-crystallised and decomposed by hydrochloric acid, this substance yields pure salicylic acid, having identical properties with that obtained from winter-green oil (see page 144). If the mother liquor from the salicylate of calcium be further concentrated, another crop of impure crystals may be obtained. There remains in solution a very soluble cresotate of calcium,\* which, on decomposition by hydrochloric acid, gives a precipitate of cresotic acid. This, when crystallised from boiling water, forms silvery plates, which are much more soluble than salicylic acid in both hot and cold water. The proportion of cresotic acid in commercial artificial salicylic acid is probably from 15 to 25 per cent.

\* Excess of milk of lime cannot be substituted for the carbonate of calcium, or a sparingly soluble basic calcium cresotate results, which cannot be separated from the salicylate.

Methyl cresotate is a fragrant liquid exactly resembling, and produced in a similar manner to, methyl salicylate.

The violet reaction with ferric chloride is common to both salicylic and cresotic acids.

**Oxybenzoic Acid** \* and **Para-oxybenzoic Acid** are isomers of salicylic acid (meta-oxybenzoic acid), which are said to be sometimes present in commercial samples of the latter. The following table shows the chief differences of analytical value :—

	Oxy-benzoic Acid.	Para-oxybenzoic Acid.	Salicylic Acid.
Fusing point.	(?)	210° C.	125° C.†
Solubility in water at 0° C.	1 in 265.	1 in 580.	1 in 1100.
Volatility. " at 15° C.	...	1 in 126.	1 in 1000.†
	Not volatile with the vapour of water.	Not volatile with the vapour of water.	Volatilises with steam when the solution is distilled.
Reaction with ferric chloride.	None.	Yellow precipitate, soluble in excess.	Deep violet colour.
Antiseptic properties.	None.	Strong.	Strong.

Salicylic acid may be partially separated from para-oxybenzoic acid by mixing the hot aqueous solution with excess of milk of lime, when a basic calcium salicylate separates on cooling. A more exact separation may be effected by drying the free acids at 100° C., and agitating with anhydrous chloroform. Salicylic acid dissolves readily, but para-oxybenzoic acid remains chiefly undissolved.

Salicylic acid forms a well-defined series of salts, of which some have been used in medicine. The sodium salt is the best known.

**Sodium Salicylate** is a white crystalline powder, soluble in an equal weight of water, only slightly soluble in absolute alcohol, but soluble in 8 parts of rectified spirit. Both the alcoholic and

\* According to the most recent researches, it appears that salicylic acid is really the true ortho-oxybenzoic acid, and that the so-called oxybenzoic acid is the meta-modification. I have thought it best to retain the ordinary nomenclature.

† The high melting point of some samples of salicylic acid, is probably generally due to an admixture of cresotic acid. According to Bourgoin, 1 part of salicylic acid is soluble in 444 parts of water at 15° C.

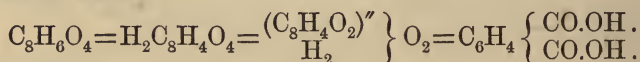


the aqueous solution give a violet colour with ferric chloride. On ignition, sodium salicylate leaves 33·3 per cent. of  $\text{Na}_2\text{CO}_3$ . It is completely soluble in ammonia, and the solution does not reduce nitrate of silver, even on boiling. Barium chloride should cause no precipitate in the aqueous solution, and the precipitate with nitrate of silver should completely dissolve on addition of nitric acid and alcohol.

**Sulpho-salicylic Acid** is obtained by the action of sulphuric upon salicylic acid. Its salts have received a limited application in medicine.

## PHTHALIC ACID.

**Naphthalic Acid. Alizaric Acid. Mono-carbo-benzoic Acid.**



Phthalic acid is a product of the action of nitric acid on naphthalene, alizarin, purpurin, and mungistin. Oxalic acid is formed simultaneously, and may be separated by crystallising the phthalic acid from hot water. Phthalic acid is prepared on a commercial scale (for the preparation of benzoic acid) by treating naphthalene dichloride with hydrochloric acid and potassium chlorate. It may also be obtained by several other reactions.

Three isomeric modifications of phthalic acid are known. Ordinary or *ortho*-phthalic acid is obtained as above described. *Meta*- or *iso*-phthalic acid, and *para*- or *terephthalic acid* are the other varieties.

Phthalic acid crystallises in white nacreous laminae, or shining monoclinic prisms. It melts at about  $182^\circ \text{C}$ ., and at a higher temperature loses water and volatilises as phthalic anhydride,  $\text{C}_8\text{H}_4\text{O}_3$ , which on boiling with water reproduces phthalic acid.

Heated with a single equivalent of lime, phthalic acid yields benzoate and carbonate of calcium,  $2\text{C}_8\text{H}_6\text{O}_4 + 2\text{CaO} =$

$\text{CaCO}_3 + \text{Ca}(\text{C}_7\text{H}_5\text{O}_2)_2 + \text{H}_2\text{O}$ . With a larger proportion of lime or other strong base, phthalic acid yields benzene,  $\text{C}_8\text{H}_6\text{O}_4 + 2\text{CaO} = 2\text{CaCO}_3 + \text{C}_6\text{H}_6$ .

Phthalic acid requires 120 parts of cold water for solution, but dissolves more readily in hot. It is readily soluble in alcohol, ether, and benzene; and is extracted from its aqueous solutions by agitation with either of the two last solvents.

## ERRATA.

- Page 33, line 17, *for* “.00651 of KCy,” *read* “.01302 grammes of KCy.”
- Page 34, line 10, after word “employed,” *insert* “the same quantity of the alcoholic solution of bitter-almond oil may be used.”
- Page 36, line 9, *for* “.110·2 of free KCy,” *read* “.130·2 of free KCy.”
- Page 128, line 10, *for* “Reichart,” *read* “Reichardt.”
- Page 148, lines 3 and 13, *for* “Ænanthic ether,” *read* “Ænanthic ether.”
- Page 161, Table, *for* “Ethyl nitrate,” *read* “Ethyl nitrite.”
- Page 176, line 21, *for* “ $\text{C}_2\text{HCl}_3\text{O}, \text{H}_3\text{O},$ ” *read* “ $\text{C}_2\text{HCl}_3\text{O}, \text{H}_2\text{O}.$ ”
- Pages 108, 163, 168, 174, 185, 197, 229, *for* “Fehling’s solution,” *read* “Fehling’s solution.”

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